

AD651294

NRL Report 6498

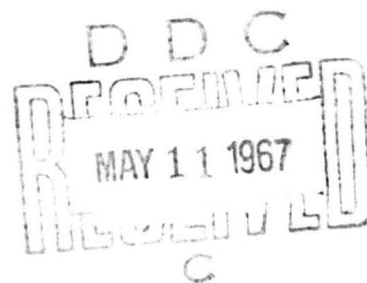
Microvoids in Glass-Filament-Wound Structures: Their Measurement, Minimization, and Correlation with Interlaminar Shear Strength

A. G. SANDS, R. C. CLARK, AND E. J. KOHN

*Organic and Biological Chemistry Branch
Chemistry Division*

March 31, 1967

ARCHIVE COPY



NAVAL RESEARCH LABORATORY
Washington, D.C.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Abstract.....	1
INTRODUCTION	1
GENERAL TECHNICAL BACKGROUND.....	1
COMPOSITE EXAMINATION AND VOID CONTENT DETERMINATION USING THE LIGHT MICROSCOPE.....	2
Gravimetric Method for Determining Composite Void Content	3
Preparation of Composite Microscopy Specimens.....	3
Qualitative Examination of Composite Structures with the Light Microscope	5
Determination of the Void Content of Glass Reinforced Composites by Optical Means	8
Adaptation of the Systematic Two-Dimensional Point-Count Technique for Void-Volume Determination.....	8
EXPERIMENTS TO PRODUCE LOW-VOID-CONTENT GLASS-FILAMENT-WOUND NOL RINGS.....	10
Experimental Glass-Filament-Winding Apparatus Materials and Winding Conditions.....	10
Resin Impregnation of the Glass Strand at Reduced Pressure	12
Vibration of the Glass Strand.....	14
Heat Treatment of the Glass Strand	14
Combined Vacuum Resin Impregnation and Working of the Glass Strand	15
CORRELATION OF THE INTERLAMINAR SHEAR STRENGTH WITH THE VOID CONTENT OF GLASS-FILAMENT-WOUND NOL RINGS.....	17
CONCLUSIONS	19
ACKNOWLEDGMENTS	19
REFERENCES	20

Microvoids in Glass-Filament-Wound Structures: Their Measurement, Minimization, and Correlation with Interlaminar Shear Strength

A. G. SANDS, R. C. CLARK, AND E. J. KOHN

*Organic and Biological Chemistry Branch
Chemistry Division*

Abstract: Microvoids in glass-filament-wound composites are being investigated to develop a reliable research method for the quantitative measurement of void content in these structures, to develop techniques for minimizing the number of microvoids in the composites, and to determine how significantly voids affect the structural integrity of the finished composite. The NOL glass-filament-wound ring is being used as a model.

A statistical point-count method adapted from petrographic modal analysis has been studied as a quantitative means of measuring void content and tentatively appears to be a more precise, rapid, and versatile method than other techniques presently being used, especially at low-void-content levels (<1 vol-%). Low-void-content (<1 vol-%) filament-wound NOL rings have been fabricated by a continuous single-strand-winding process and resin impregnation at reduced pressure with the vacuum applied only to the resin bath. Working of the strand during the resin impregnation step by various configurations of guide rolls and strand vibrating devices either at atmospheric or reduced pressure was relatively ineffective in decreasing void content as compared with vacuum resin impregnation alone. Regression correlation analysis studies have shown that a linear inverse relationship exists between the interlaminar shear strength and the void content of NOL rings and that void content is the primary factor influencing interlaminar shear strength. The high degree of correlation between interlaminar shear strength and void content derived from the statistical regression correlation analysis is indirect supporting evidence that the point-count method for the quantitative measurement of the void content of composite structures has a relatively high degree of precision.

INTRODUCTION

The investigation of microvoids* in glass-filament-wound structures has three principal objectives:

1. The development of a reliable research method for the quantitative measurement of void content in glass-filament-wound structures; in particular, a method accurate at very low void contents;

2. The development of techniques for minimizing voids in these composites;

3. The correlation of void-content with certain mechanical properties of the glass-reinforced-plastic (GRP) structure to determine how significantly voids affect the structural integrity of the finished composite.

The NOL glass-filament-wound ring is being used as a model in this investigation since it is

simple and is one of the most widely accepted industry "standards." Initially, single strand winding is being used so that the several variables may be more easily observed. The winding apparatus was designed as simply as possible consistent with proper quality control.

Following the next section this interim report is written in three main sections which describe the progress made toward partial fulfillment of each of the above three objectives.

GENERAL TECHNICAL BACKGROUND

The state of the art of fabricating glass-filament-wound structures has advanced to the stage where the elimination of large voids has become less of a problem if proper quality control is practiced in the winding process. On the other hand, the presence of microvoids has largely been ignored until relatively recently. That such imperfections may contribute significantly to composite failures has now been recognized as the result of work by Paul and Thomson (1), Hand (2), and Fried (3). Bascom (4) has demonstrated that microvoids are

NRL Problem C03-19; Project SF 020-04-01-1008. This is an interim report; work on the problem is continuing. Manuscript submitted October 11, 1966.

*For the purpose of this report, a microvoid is defined as a void having an average cross-sectional diameter of less than 50μ (0.05 mm).

inherent in the glass-filament-winding process and that these result from entrapment of air in the interstitial spaces between the filaments. The air is not displaced by the resin binder because of the high resistance to flow of the resin along and between the filaments owing to poor wetting of the filament surface by the resin. These thin interstitial voids are particularly deleterious, since they generally have very short radii of curvature at their ends; because of this sharp curvature they act as regions of stress concentration from which cracks can initiate as a load is applied to the material (Ref. 4, p. 11 of Part 1).

The structural properties which appear to be most influenced by voids, as indicated in the limited literature to date, are interlaminar shear strength and compression strength. Hand (2), using flat, 2:1 orthogonally-filament-wound panel specimens, found that interlaminar shear strength exhibits a linear, inverse relationship to void content within the "zero" to 6 vol-% void range he investigated. The void content was determined by an ultrasonic method.

Fried (3) showed that a similar relationship existed between the void content and the compression strength of orthogonal composite materials. Consistently high interlaminar shear strengths (12,700 psi) were obtained by Paul and Thomson with filament-wound NOL rings fabricated in a moderate vacuum (ca. 10 mm Hg) by enclosing the whole winding operation in a vacuum chamber. A high degree of transparency was also exhibited by these specimens which was attributed to low void content.

Adequate evidence is presently not available, but other composite properties are undoubtedly affected by void content. One important example may be fatigue life, which is dependent on multiple variables involving stress and/or strain. An important variable in the fatigue process is the presence of stress concentrators (5), and voids are a well-known variety of this category.

The correlation of void content with the mechanical properties of a composite is presently limited in part by the inability to determine accurately the void content, particularly at low void levels. Usually the void content is calculated gravimetrically, on the basis of density and glass content determined by ignition. Procedures based on ultrasonic attenuation and x rays are used less extensively because of the rather elaborate equip-

ment required. However, it is believed the resolution of the latter two methods probably is too low to even detect the microvoids with which this report is primarily concerned, unless a large number are grouped together. The shortcomings of the gravimetric method will be discussed later. In spite of the limitations of these methods, references are made in the literature to "void-free" or "zero-void" composites, and even negative volume-percent void contents are cited. It is doubtful if any of these structures are void-free with respect to microvoids, as a careful microscopic examination of thin sections would probably reveal. Several "void-free" composites examined at this Laboratory contained numerous microvoids, although the total void content was low compared with the amount usually found in similar structures.

Efforts are being directed, therefore, to derive a precise, accurate research method for determining very low void contents in these structures. Since the distribution and type of void are also important for understanding the role of voids in relation to mechanical properties, statistical optical counting techniques similar to those used in petrography and metallography are currently being investigated as one approach to solving this problem.

COMPOSITE EXAMINATION AND VOID CONTENT DETERMINATION USING THE LIGHT MICROSCOPE

The light microscope is a versatile research tool with which valuable information regarding the fine structure of glass-reinforced epoxy composites may be obtained (6). If the specimens are prepared properly, then filament size and packing, resin distribution, and defects such as voids, foreign materials, and crossed filaments can be observed and studied. In addition to qualitative information gained from the examination of the composite structure, light microscopy offers a potential means for quantitatively determining the void content. Both the qualitative and quantitative applications of light microscopy will be presented after a brief discussion of some of the shortcomings of the gravimetric method, which is most commonly used for void content analysis. As will be shown, the precision of the gravimetric method, particularly with composites having low void contents, is inadequate to define the void

content accurately for correlation with a mechanical property.

Gravimetric Method for Determining Composite Void Content

The gravimetric method for determining the void content of glass reinforced composites is calculated from the density, and glass content obtained by ignition, using (6) the equation

$$\text{vol-\% voids} = \frac{\rho_r \left(1 - \rho \frac{W_g}{W}\right) - \rho \left(1 - \frac{W_g}{W}\right) \times 100}{\rho_r - \rho_a}$$

where

ρ_r = density of resin

ρ = density of composite

ρ_g = density of glass

ρ_a = density of air (considered zero)

W = total weight of sample

W_g = weight of glass after ignition.

The precision of the method is probably adequate for composites containing a relatively high volume percent of voids, but when used for the determination of void content in the range 0 to 1.5 vol-%, the input values available and experimentally derived for some of the terms in the equation are not sufficiently accurate to provide void-content values that are outside the experimental error of the method. The uncertainty of the glass density ρ_g which may vary from 2.48 to 2.50 introduces a possible error of ± 0.5 vol-% depending on which values are chosen. Great care must be used in determining the composite density ρ , since it is determined by weight differences in air and water, and problems of complete wetting of the specimen surface and penetration of pores and flaws by the water may readily introduce errors. The presence of foreign material which is not removed by ignition and is included in the weight of glass W_g introduces additional error. Although some of the errors may cancel each other, in some cases they may be additive. There

is no way of knowing exactly the total error contributed by these defects in the gravimetric method for determining void content, but a conservative estimate indicates a possible error of at least ± 1.0 vol-%. Other techniques of determining void content, as mentioned earlier, are also limited when determinations of very low void content are required. The investigation of petrographic modal analysis techniques, to be discussed as part of this section of the report, is an attempt to find a more accurate method of determining the void-content of glass-filament-wound composites when very low values are involved.

Preparation of Composite Microscopy Specimens

The specimens for microscopic examination were prepared from segments cut from a glass-filament-wound NOL ring for interlaminar shear measurements using the horizontal beam method. The segment was mounted in Blocking Wax No. 48* on a microscope slide and 10-to-20-mil-thick cuts were made with a diamond saw: several in the cross-sectional or normal-to-the-fiber direction and several in the transverse or parallel-to-the-fiber direction (Fig. 1). After removal of the wax the cut specimens were mounted on the bed of a surface grinder using double-coated adhesive tape and were ground. The transverse specimens were ground to 4 to 5 mils in thickness and the cross-sectional specimens to 10 mils. The specimens disintegrated when attempts were made to grind below these thicknesses because too little resin binder remained to hold the glass filaments together. After grinding, surface contaminants were washed away with water and alcohol. For only a quick estimate of the degree of void inclusion or for rough comparison with other specimens, segments were cut into thin slices with a hand saw and sanded smooth with 400 silicon carbide paper.

Further polishing of the specimens was unnecessary, since cuts, scratches, and other surface imperfections that fine polishing would eliminate were masked by applying a thin film of isopropylbiphenyl to the specimen surface before viewing under the microscope. The effectiveness of this treatment is illustrated in

*Universal Shellac Company, 540 Irving Avenue, Brooklyn, N.Y.

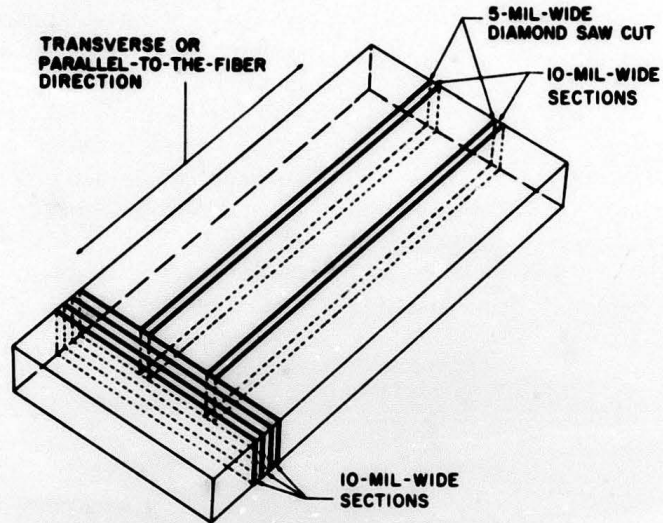
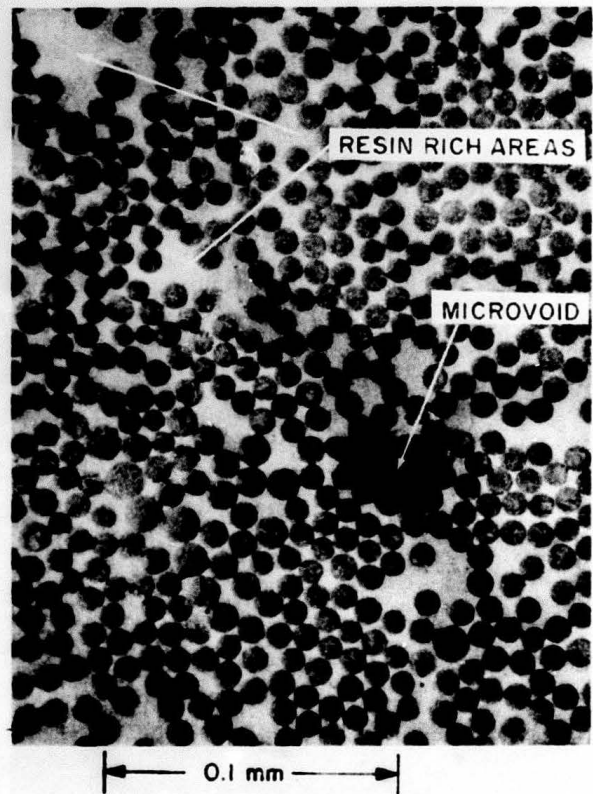


Fig. 1 - Schematic drawing of the thin sectioning of an NOL ring segment for light microscopy examination



(a) a section before application of isopropylbiphenyl



(b) the same section after application of isopropylbiphenyl

Fig. 2 - Photomicrographs of glass-filament-wound-composite cross section showing the effectiveness of a thin film of isopropylbiphenyl in masking surface imperfections (450X)

Fig. 2. Any low-viscosity liquid which has a refractive index approximating that of the resin and will not react with it would probably work as well, since the function of an applied film is to reduce light scattering by the rough surface of the specimen (4).

Qualitative Examination of Composite Structures with the Light Microscope

The microscopy equipment used in this work was an American Optical Co. trinocular microscope, Model XL-10TG-QW, equipped with a 4 by 5 in. Grafflok camera back and Polaroid Land film holder No. 500. Polaroid Polapan Type 52 film was found to give the best results in the photography.

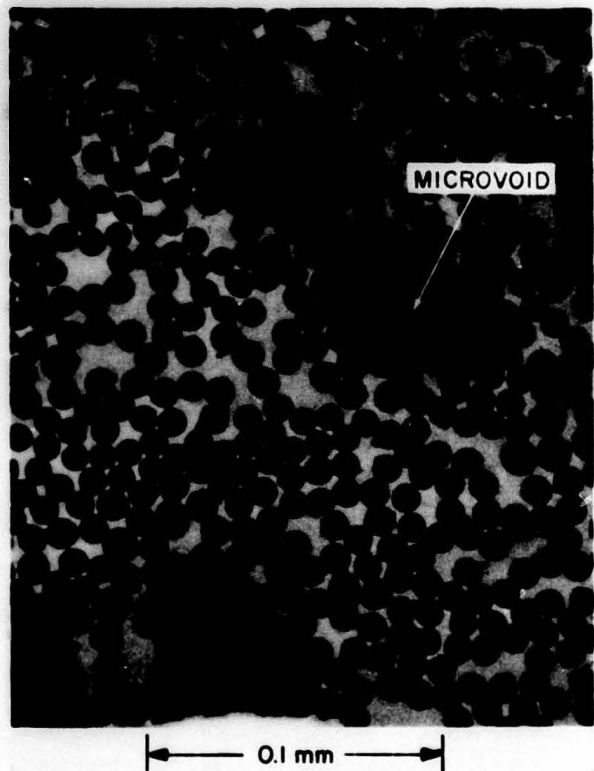
For most of the studies transmitted light was used which gave a bright-field, high-contrast image. An oblique reflected light was used occasionally, which produced a dark field image, but the contrast was inferior to that obtained with transmitted light.

Paul and Thomson (1) have roughly classified voids found in glass-reinforced-plastic composites into four categories: general, interstitial, planar, and craze voids. Essentially, they were grouped on the basis of their origin and to a lesser extent on their size, whereas in this investigation the average cross-sectional dimension of the voids was used as the criterion of classification. Application of careful quality controls in winding the NOL rings and the various techniques used for minimizing voids, essentially limited them to small or microvoids which corresponds to the interstitial and the lower size range of the general categories of Paul and Thomson. Craze voids or cracks, which result when the composite structures are highly stressed may occur in the fatigue studies associated with this project, but that phase of the program will not be discussed in this report.

Figures 3(a) and 3(b) represent typical photomicrographs of transverse and cross-sectional specimens, respectively. These were chosen to show the different types of voids as well as typical



(a) Transverse section (100X)



(b) Cross section (450X)

Fig. 3 - Photomicrographs of typical thin sections of glass-filament-wound NOL ring segments

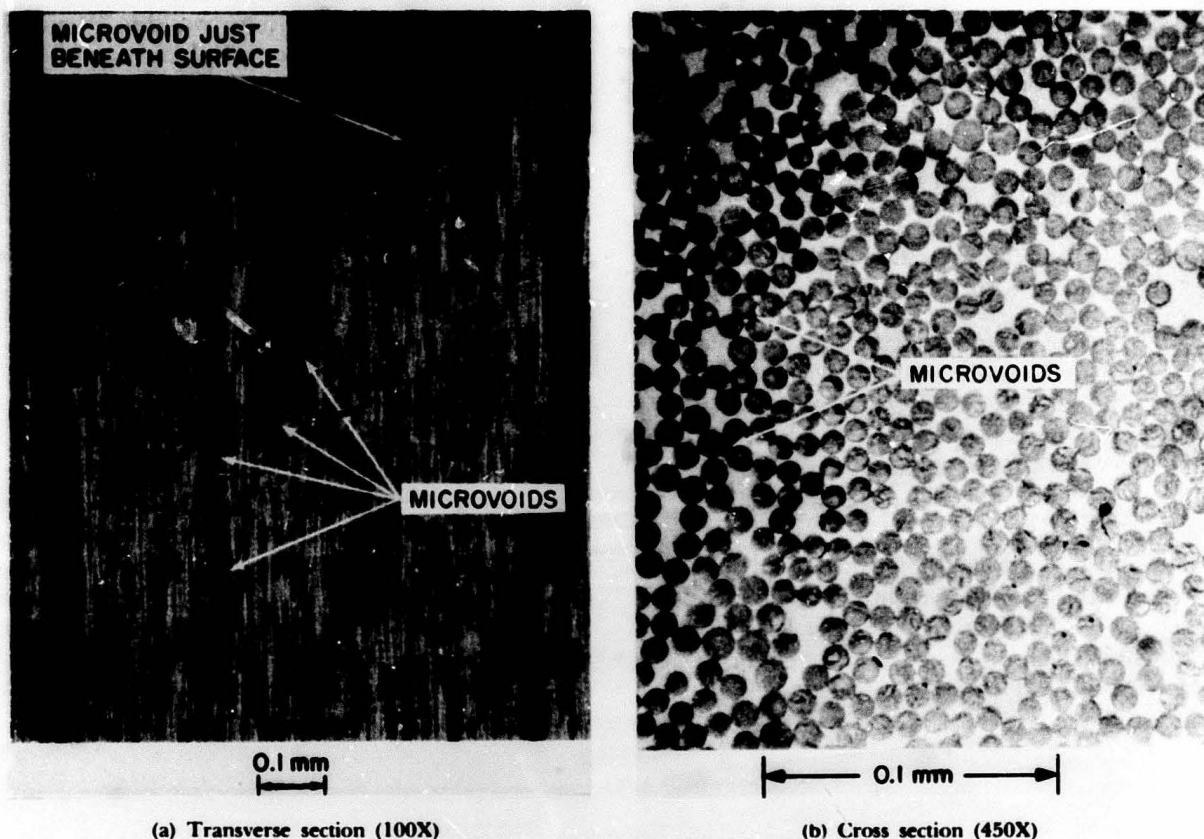


Fig. 4 — Photomicrographs of thin sections of NOL rings which, in comparison with the sections of Fig. 3, shows the effect on the void content and packing of glass filaments of increased winding tension (180 g as compared with 130 g in Fig. 3) and resin impregnation of glass strand at reduced pressure.

structures comprising the NOL rings. Figure 4 illustrates the change in structure and void size when the ring is wound at higher tensions and the strand is resin impregnated at reduced pressure. Some of the voids may lie just below the surface, but these can be brought into view by slightly changing the focus of the microscope. Manipulation of the focal plane can also be used to distinguish between true voids and foreign material imbedded in the resin matrix. In addition to voids, cross-sectional specimens may be used to determine glass-filament diameters, glass-filament distribution and number, resin-rich areas, and foreign materials.

Ordinarily the microvoids are about two to three times the diameter of the filament itself. However, microvoids have occasionally been observed as small pockets of air, seemingly attached to the glass filaments, which are smaller in diameter than the glass filament (Fig. 5). The origin of these flaws is uncertain.

All of the components of a filament-wound composite are potential sources of voids or flaws. Reference has been made to the interstitial spaces between the filaments as one source of voids. However, the coated filament itself appears to contain voids which probably are formed when the filament finish is applied. These can be seen as minute bubbles in the coating, as shown in the photomicrographs in Fig. 6. This sort of flaw is almost impossible to correct, since the encapsulated air cannot be replaced by the resin binder unless the finish happens to be readily soluble in the resin. How deleterious these minute voids may be to the structural strength of the composite is not known.

Microscopic examination has also revealed other defects besides voids in the glass strand which represent a potential source of structural weakness, namely, foreign material lodged between or attached to the glass filaments. Figure 7(a) shows what is believed to be a glass chip lodged between several filaments of a strand. Whatever the

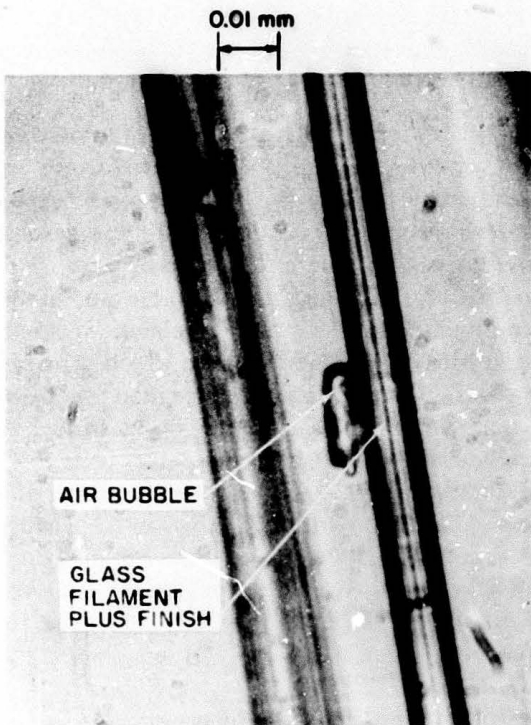


Fig. 5 - Photomicrograph of an air bubble attached to glass filament (1000X)

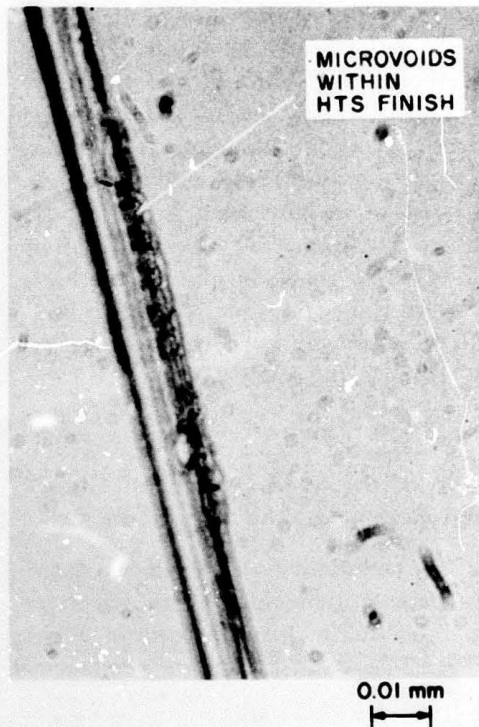


Fig. 6 - Photomicrograph of occluded voids in the HTS finish of an S-glass filament (1000X)



(a) Foreign body in glass strand



(b) Same type material showing the ineffectiveness of a burn-off at 1200°F in removing a foreign body

Fig. 7 - Photomicrographs of foreign bodies (perhaps glass chips) lodged between the glass filaments of a strand

composition, this type of foreign particle was not removed by ignition at 1200°F (Fig. 7(b)). Such foreign bodies were found to be fairly common throughout the several packages of yarn examined. Broken filaments were also quite evident throughout these filament packages. These and other variables, such as the reproducibility of winding test specimens, and the precision of the mechanical test methods all combine to present a rather complex situation to analyze when attempting to correlate void content with a mechanical property of a composite.

Determination of the Void Content of Glass Reinforced Composites by Optical Means

Modal analysis techniques have been used for many years by petrographers and metallographers for estimating the volume constituents of rocks and metals (7). The composition of a material expressed in terms of the relative amounts of constituents actually present is called a mode. The procedures by which the compositions are determined is called modal analysis. Nearly all modes are estimated by areal measurement performed on thin sections under the microscope. Although there are a number of variations, they are based on one of two methods to obtain a reliable estimate of the relative proportions of the measurement area and hence the volume (7) occupied by components of different species: by adding the intercept lengths for each species along a set of parallel equidistant lines, or by counting the number of points in a symmetrical grid which are underlain by each species. These are the line segment, or lineal analysis, and the point-count techniques. Hilliard and Cahn (8) treated five methods of metallographic analyses and concluded that the most efficient method was a systematic two-dimensional point count. Both the line-segment and point-count techniques have been applied to the volume fraction analysis of voids in filament-wound composites. The point-count method was found to be faster and less tedious, so efforts have been concentrated on developing this method as a means of determining volume void content.

Adaptation of the Systematic Two-Dimensional Point-Count Technique for Void-Volume Determination

The line intersections of a grid superimposed on an area of the specimen under a microscope are the points under which the count is made. A net micrometer disk 10 mm square in the eyepiece of the microscope covered a specimen area with 100 points. A void which fell under any point was counted (Fig. 8). A magnification of 450X was used for counting microvoids, which provides a grid coarse enough that not more than one point falls on a void, a necessary condition according to Hilliard and Cahn (8). After the points with voids under them in a given area were counted, the specimen was moved horizontally by a vernier adjustment of the microscope stage and the count repeated in a new area. In this manner a *line* of ten grids, or 1000 points, was superimposed on the specimen and the voids falling under the points totaled.

The volume percent of voids is

$$\frac{100 P_v}{P_t}$$

where P_v = number of points falling on voids

P_t = total number of grid points.

The precision of the method has been studied by Howard and Cohen (9). They show that the number of measurements necessary to achieve a

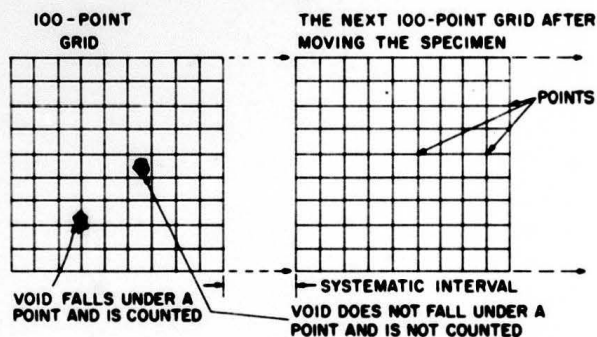


Fig. 8 — Schematic diagram showing the point-count technique for the determination of void content in GRP composites

95% confidence level, so that the *error of the mean* will not exceed $\pm 1\%$, may be calculated from the equation

$$N_{95\% \pm 1\%} = 4V_x = 4s^2$$

where V_x = variance

s = standard deviation.

Similarly*

$$N_{95\% \pm (1/4)\%} = 64 V_x.$$

*Derived by B. N. Navid and J. P. Grimes, Mathematical Physics Branch, Solid State Division, NRL.

These equations represent the precision with which measurements are made and not necessarily the accuracy. A large error could enter the measurements because of bias or some other reason; the results would be as precise as the equation predicts but not accurate. The precision increases with the number of traverses or grids measured. A typical point count of voids in an NOL ring segment and the calculations of the volume percent of voids, standard deviation, $N_{95\% \pm 1\%}$, and $N_{95\% \pm (1/4)\%}$ are shown in Fig. 9.

This method of determining the volume percent of voids in glass-filament-wound composites is

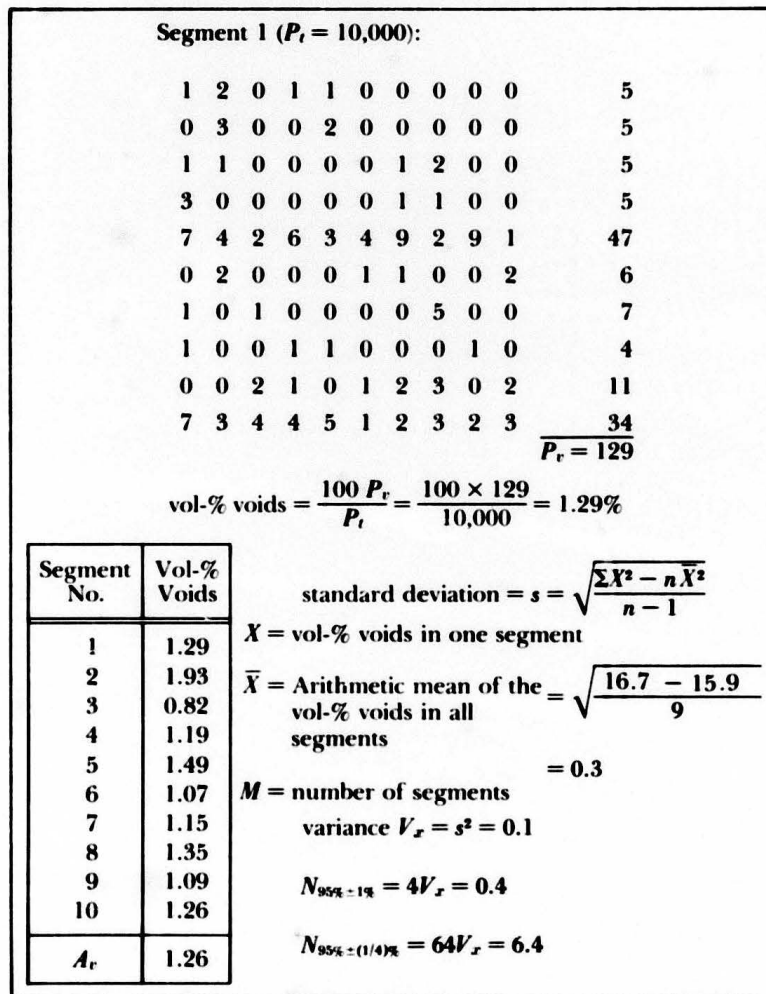


Fig. 9 — Procedure for calculating the volume percent of voids using the systematic point-count modal analysis method (NOL Ring. No. NRL-14)

presently being studied by NRL statisticians in an attempt to ascertain the accuracy of the measurements, including the number of grid points and number of specimens necessary to achieve a given accuracy. Tentative results of this study indicate that if uniform randomness of void distribution in the specimen is assumed, the $N_{95\%}$ confidence level $= 4V_r$ for obtaining 1% precision or the $N_{95\%}$ confidence level $= 64V_r$ for obtaining 1/4% precision may be applied to the number of grid points measured and not the number of specimens. This implies that only one specimen need be measured, provided the void distribution and specimen selection is truly random.

EXPERIMENTS TO PRODUCE LOW-VOID-CONTENT GLASS-FILAMENT-WOUND NOL RINGS

Experimental Glass-Filament- Winding Apparatus

The single-strand experimental glass-filament-winding apparatus used for fabricating the NOL rings is shown in Figs. 10 and 11. The glass strand milk-bottle spool (Fig. 11(a)) is vertically mounted

on the shaft of a General Electric CR-9540 hysteresis brake, which provides variable tension control to the strand as it travels over guide pulleys to a 14-in.-long, 3-in.-wide, 2-1/2-in. deep, glass resin impregnation boat (Fig. 11(b)). Tension on the strand is further controlled as it leaves the impregnation bath by passing it over a guide pulley attached to the shaft of another hysteresis brake. The strand is guided onto the ring mandrel (Fig. 11(c)) by passing it through a slot cut in a nylon spool which is moved in a horizontal reciprocating motion by an off-center cam. The reciprocating speed of the level winder is synchronized with the rotating speed of the mandrel so that the strand is laid down evenly as the winding proceeds. The simple arrangement of the apparatus permits easy observation of any part during a winding operation and facilitates modifications and alterations.

Materials and Winding Conditions

The resin system used was Epon 826/Methyl Nadic Anhydride (85 phr*)/benzyl dimethylamine

*Parts per hundred parts of resin.

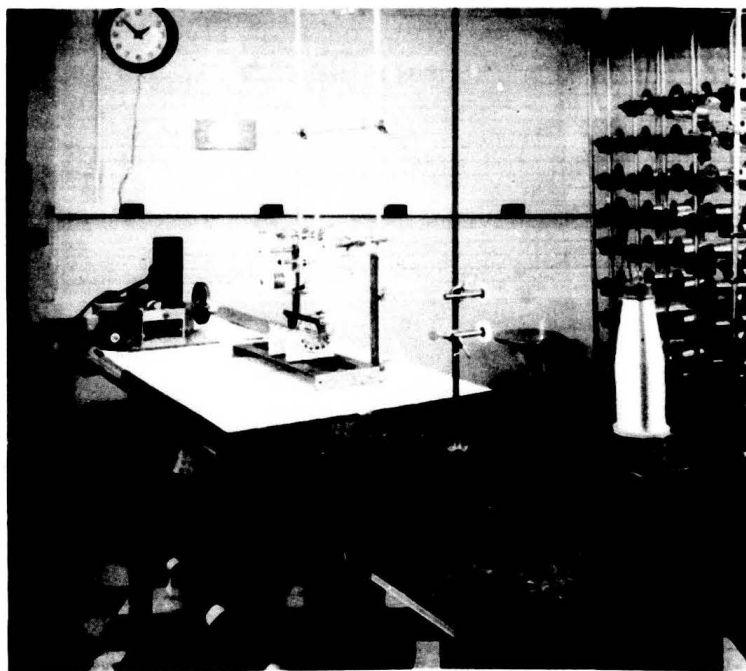
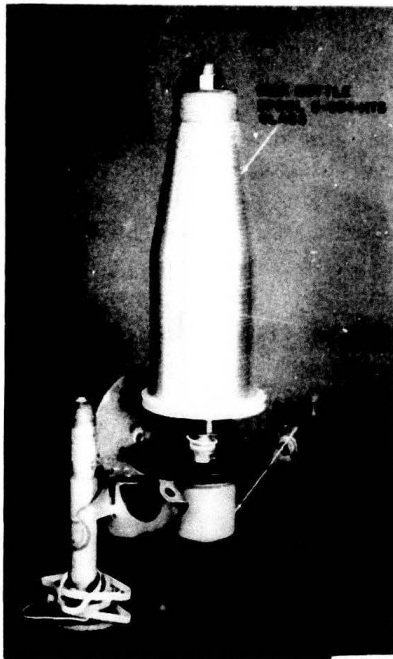
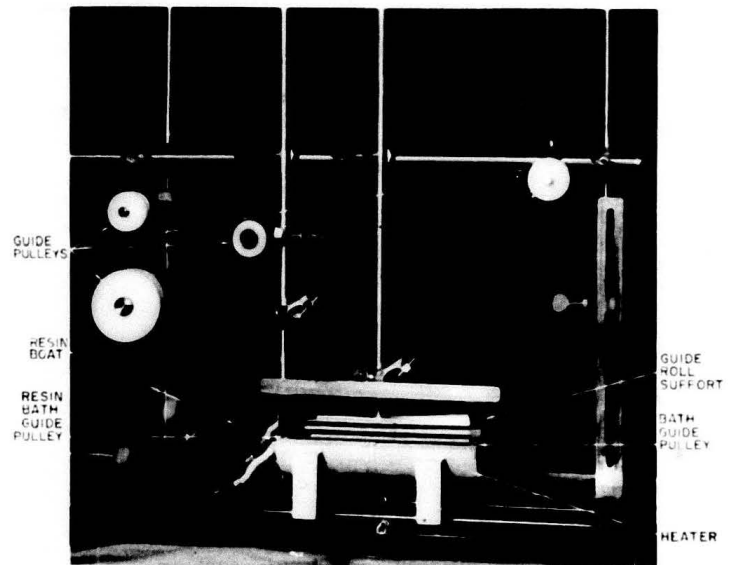


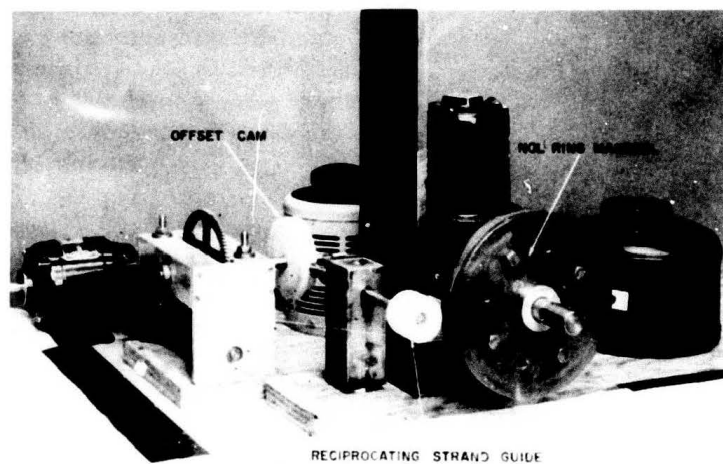
Fig. 10 — Overall view of an experimental single-strand NOL glass-filament-winding apparatus



(a) Mounting and brake with a milk-bottle spool feeding out the glass strand



(b) Resin impregnation boat



(c) Level winder assembly and NOL ring mandrel

Fig. 11 - The main components of the experimental single-strand NOL ring glass-filament winding apparatus shown in Fig. 10

(1 phr). The composites were cured for 2 hours at 110°C, 2 hours at 140°C, and 2 hours at 175°C. Before winding, the resin was filtered and then was deaerated on a modified Rinco evaporator system described in an earlier report (10). During winding, the resin temperature was maintained at 54°C by means of a resistance heater shaped to follow the outside contours of the resin boat.

The glass filament reinforcement used was Owens-Corning Fiberglas S-994 HTS coded SCG 150/1/01 $\times$ 901-994. Except during actual winding operations, the spools were stored in polyethylene bags in a refrigerator at -10°C.

Initial studies using the experimental winding system were directed toward finding the optimum strand tension and resin bath temperatures. Strand tensions measured with a Kidde-Sipp tensiometer were varied from 50 grams to 130 grams. A tension of 130 grams appeared, from microscopic examination and glass-content determinations, to give the greatest uniformity of structure with respect to resin and filament distribution and was selected as the standard winding tension. Subsequent additions to the winding train and other modifications caused changes in the winding tension at various times and are so designated. Variations in resin bath temperature from 43°C to 81°C apparently had little effect on the final ring structure or the winding process, so 54-55°C was arbitrarily designated as the standard resin bath temperature.

Resin Impregnation of the Glass Strand at Reduced Pressure

Paul and Thomson (1) first demonstrated that when the whole winding system was enclosed in a chamber and cylinders were wound at reduced pressure, composites were produced which had low void content and exhibited consistently high interlaminar shear strength values. Microscopic examinations showed the presence of microvoids in low concentrations as compared to similar structures wound at atmospheric pressure. However, fabricating large structures in such a vacuum system presents formidable engineering problems, so efforts on this project have been directed toward winding NOL rings with only the resin impreg-

nation pot at reduced pressure, which, if successful in producing low-void structures, might be practical for large-scale operations.

The vacuum resin-impregnation chamber is shown in Fig. 12. A 2000-ml three-necked resin reaction flask fitted with capillary tubes which served as entrance and exit ports for the glass strand was first used as a resin impregnation pot. A Megavac pump was attached to the center neck of the flask. The strand was guided horizontally through the bath by two small nylon guide rolls, and a slit rubber wiper located just under the capillary exit port removed excess resin from the strand as it left the resin bath. With this arrangement a vacuum of 5 mm Hg was obtained in the resin chamber. However, air drawn down through the exit capillary port created many fine bubbles in the resin which adhered to the strand as it came through the capillary. The resin pot pressure was reduced to 3 mm Hg by attaching to both entrance and exit ports a vacuum roughing chamber consisting of capillaries and glass cylinders through which the strand passed and to which other vacuum lines were attached. Hence, the air drawn through the strand exit capillary was greatly reduced, which alleviated the bubble formation in the resin as the strand passed through the exit capillary.

The 50-gram tension on the strand before it entered the resin chamber increased to 180 grams as a result of passage through the system, and the rings were wound at this increased tension. Obviously, at this higher tension the glass content of the composite was increased.

Data summarizing the effect of vacuum resin impregnation of the glass-wound reinforcement on void-content and interlaminar shear strength for four NOL rings fabricated with this equipment are shown in Table 1.

Ring 15, the control, was wound under the same conditions as the other four rings except that the resin was impregnated at atmospheric pressure. It is believed the relatively low void content and higher interlaminar shear values in comparison with those usually obtained in standard winding is attributed to the higher winding tension which may tend to "press out" some of the voids. The increase in winding tension also gives a more compact structure with increased glass content and fewer resin-rich areas.

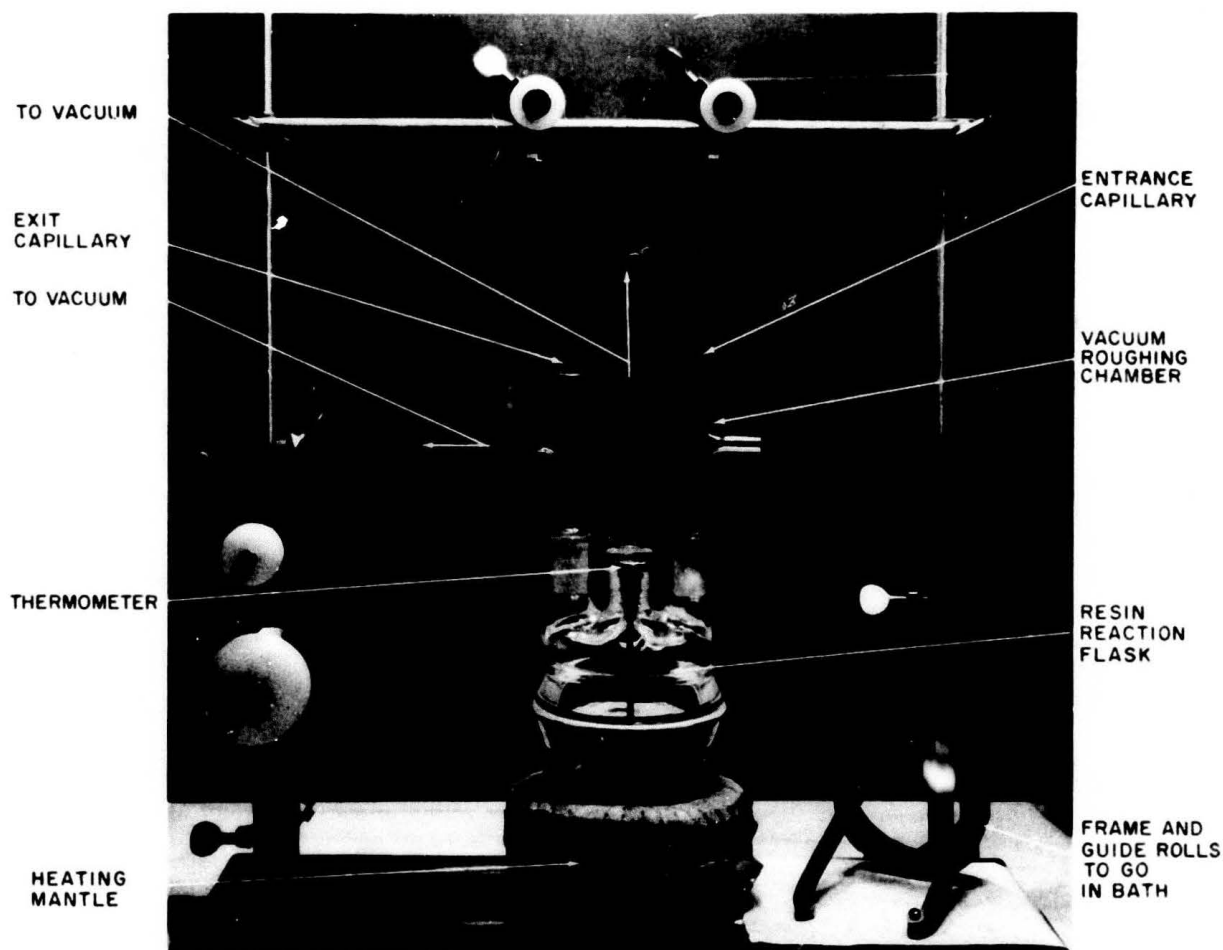


Fig. 12 — Reaction vessel for resin impregnation of the glass strand at reduced pressure

TABLE I
Void Content and Interlaminar Shear Strength of NOL Rings
Fabricated from a Glass Strand
Impregnated with Resin at a Chamber Pressure of 3 mm Hg*

NOL Ring Number	Glass Content (wt-%)	Void‡ Content (vol-%)	Interlaminar Shear Strength (10^3 psi)	Standard Deviation (psi)	Coefficient of Variation (%)
15†	82.9	2.4	11.4	268	2.3
14	84.8	1.6	12.7	318	2.5
23	—	1.1	13.1	435	3.3
24	85.2	0.6	13.2	365	2.7
25	—	0.4	12.9	302	2.3

*Winding tension, 180 g; resin bath temperature, 54°C.

†Control — no vacuum.

‡Determined by the point-count method.

Higher values for the interlaminar shear strength and lower void content as compared to controls wound by the standard winding process, were also obtained from rings fabricated elsewhere by a proprietary winding process (11). In this instance, the glass content exceeded the controls content by approximately 6%. However, details of the winding process are not available, and although the effect of higher glass content on void content and interlaminar shear strength parallels experience in this investigation, it is only conjecture that the observed phenomena are related.

Vibration of the Glass Strand

Bascom (4) observed in his studies on the origin and removal of microvoids in filament-wound composites that the number of voids in a strand was markedly reduced if the strand tension was fluctuated as the strand passed through the resin bath. The alternate release and application of strand tension apparently permitted the elongated microvoids to pull up into more spherical shapes and thus to be more easily detached. This

effect combined with good wetting of the glass by the impregnant gave the lowest void count. The effect was less pronounced when using an epoxy resin which had a relatively high contact angle with the HTS finish on the glass filaments and consequently poor wetting characteristics.

In order to determine if this treatment would provide a means for reducing void content and increasing interlaminar shear strength of a composite, a doorbell coil was mounted over the resin bath and the submerged strand passed through an eyelet attached to an extension of the doorbell clapper as shown in Fig. 13. This arrangement vertically oscillated the strand at a frequency of approximately 1500 cpm. However, the treatment by itself was not particularly effective, since values of 4.2 vol-% and 10,600 psi were obtained for the ring void content and interlaminar shear strength, respectively.

Heat Treatment of the Glass Strand

The glass strand is made up of 204 single, HTS-coated filaments with a strand twist of about one per inch. Many of the individual filaments appear

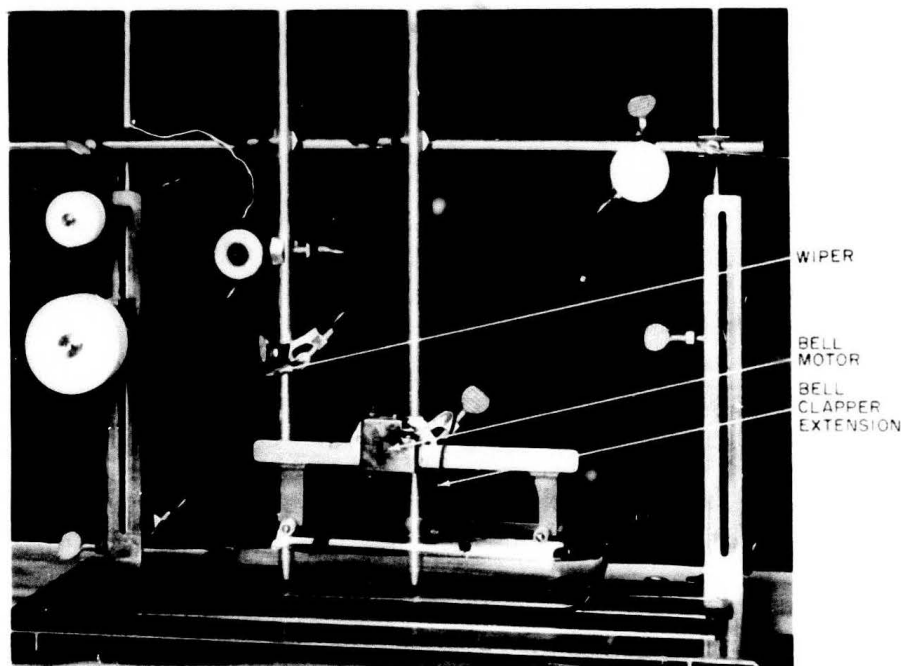


Fig. 13 — Doorbell clapper arrangement for vertically vibrating the glass strand during resin impregnation. (In actual operation the strand guide system and clapper oscillator is lowered into the resin boat.)

to be loosely bonded to each other by the HTS finish, which interferes with the complete impregnation of each filament by the resin. In addition, as Bascom has demonstrated, the high contact angle exhibited by the resin on the HTS finish further prevents filling the interstitial voids between the filaments. In an attempt to separate the filaments to assist in penetration of the resin, the strand was passed through an 18-in.-long tube heated at 285°C (547°F) just before entering the resin bath. The idea was that perhaps the filaments might be at least partially separated by melting the finish just as the strand entered the liquid resin. No improvement was noted in void content or in interlaminar shear values as a result of this treatment. Nor did any improvement result when the strand was heated in the same manner at 254°C (490°F) just before winding on the mandrel.

Combined Vacuum Resin Impregnation and Working of the Glass Strand

A vacuum chamber was constructed large enough to provide space for the resin bath, additional guide rolls, and the oscillating strand vibrator arrangement described above for working the glass strand as it passes through the resin bath

at reduced pressure (Fig. 14). One side of the chamber consisted of a 1-in.-thick piece of flat Plexiglas through which the operation could be observed. This panel was removable for access to the chamber. In principle the vacuum system and entrance and exit ports were essentially the same as used with the smaller vacuum resin impregnation vessel, except that more efficient vacuum pumps were used.

A series of winding experiments was performed to determine if a combination of vacuum resin impregnation and working of the strand during the process would decrease the void content of the resultant composite. Figure 15 shows schematic diagrams of the various configurations of guide rolls used for working the glass strand. Diagrams A, B, and C show successively increased working of the strand after passing through the resin bath while thinly coated with the epoxy resin. Diagram D depicts working of the strand in the resin bath by threading the strand back and forth through a set of guide rolls, and E is the doorbell clapper arrangement previously described.

Data derived from these experiments are shown in Table 2. Increased working of this glass strand within the vacuum chamber, at least for the arrangements described, does not appear to offer

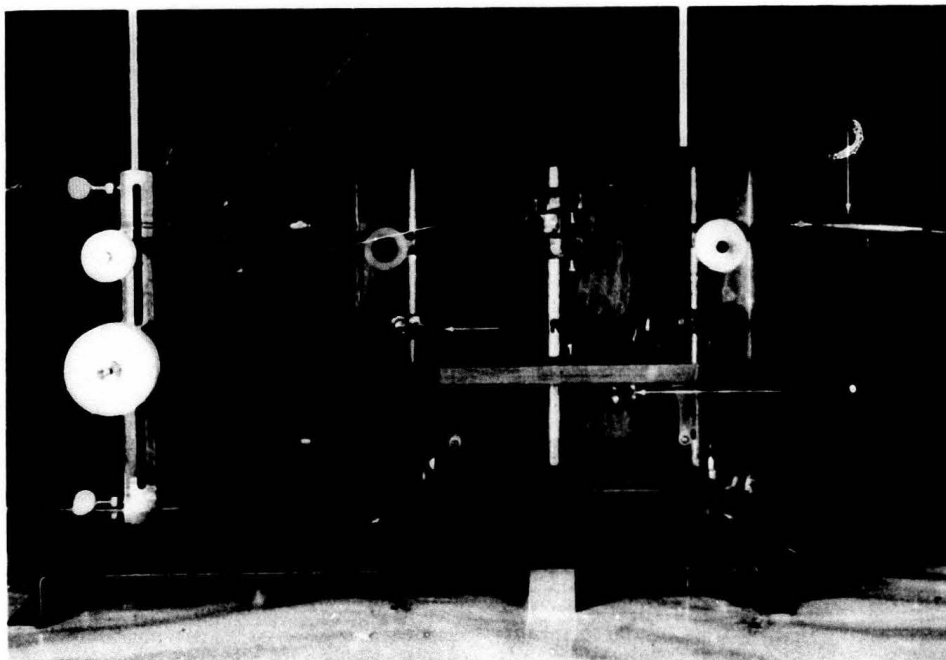


Fig. 14 - Large vacuum chamber to house the glass-strand resin-impregnation apparatus

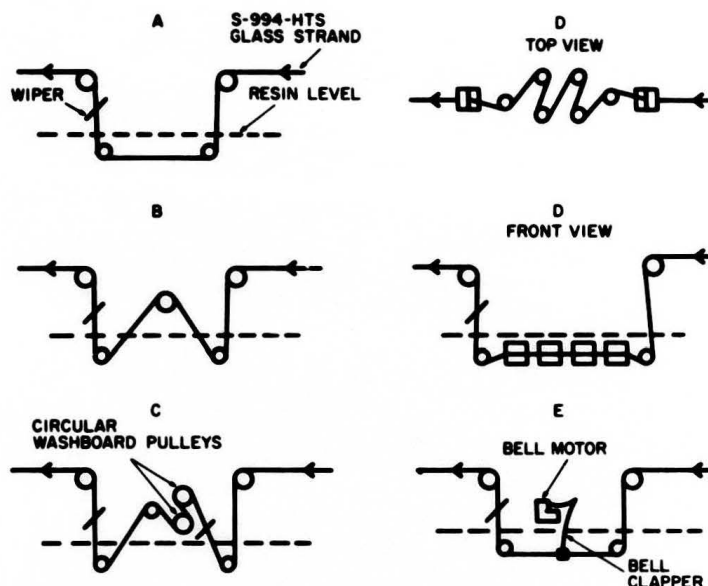


Fig. 15 — Guide-roll arrangements for working the glass strand during the resin impregnation process

TABLE 2
Void Content and Interlaminar Shear Strength of NOL Rings
Fabricated from a Glass Strand Impregnated with
Resin and Mechanically Worked in a Vacuum Chamber*

NOL Ring Number†	Winding Tension at the Mandrel (g)	Resin Vacuum Chamber Pressure (mm Hg)	Void Content‡ (vol-%)	Interlaminar Shear Strength (10 ³ psi)	Standard Deviation (psi)	Coefficient of Variation (%)
26(A)	130	0.5–0.2	0.85	12.71	318	2.8
27(B)	130	0.08–0.01	0.70	12.77	210	1.6
29(C)	160	1.0–0.8	2.18	11.87	343	2.9
30(C)	160	atm.	5.00	9.92	161	1.6
31(D)	170	0.8–0.5	1.45	12.37	385	3.1
32(D)	170	atm.	3.60	11.00	564	5.1
28(E)	130	0.5–0.35	1.1	11.89	293	2.5

*Resin bath temperature, 54°C.

†The letters in parentheses refer to the schematic diagrams in Fig. 15.

‡Determined by the point-count method.

any improvement with respect to interlaminar shear strength and void content of the rings over fabrication with vacuum resin impregnation alone. In fact, the increased working may be detrimental in some instances, as indicated by the values obtained from Ring 29(C), which was worked over

several guide rolls and two circular washboard pulleys. Also, no improvement was noted by combining the vacuum resin impregnation and vibration of the glass strand with the doorbell clapper arrangement (Ring 28(E)). Again, lower shear strength was obtained with this arrangement

than ring fabrication with vacuum resin impregnation alone. This may be because of damage to the glass strand during the oscillation treatment.

CORRELATION OF THE INTERLAMINAR SHEAR STRENGTH WITH THE VOID CONTENT OF GLASS-FILAMENT-WOUND NOL RINGS

Reference was made earlier to the linear inverse relationship which Hand (2) has demonstrated exists between interlaminar shear strength and void content of flat 2:1 orthogonal laminates. In order to establish the relationship which exists between interlaminar shear strength and void content of glass-filament-wound NOL rings, a statistical linear regression correlation analysis was performed on the data listed in Table 3. These

data were derived from eighteen rings covering a range of void content values from 5.2 to 0.16 vol-% and a range of interlaminar shear strength values from 9850 to 13,980 psi. The glass content in this series varied from 75 to 86 wt-%.

Common to all of the rings are the resin and glass systems shown in the table note. The rings were wound by a variety of diverse winding processes, which might be expected to introduce variables influencing the correlation. For example, JR-1, JR-2, and JR-4 were dry wound on a Lamtex winding machine using 18 strands and were vacuum resin impregnated *in situ*, or batchwise, then cured. The Mc#7 ring was one of a set fabricated by a proprietary winding process which produces rings having low void contents (11). The details of this process are not known, except that no vacuum is involved. The rest of the series were wound on the experimental single strand winding equipment that was described in this report in the course of experiments directed toward minimizing the void content of the composites. The process variations included vacuum resin impregnation, mechanical working of the strand over guide rolls and pulleys, and strand vibration. From this it is obvious that no attempt was made in the selection of the specimens to restrict the number of variables involved.

The correlation coefficient r for this series was calculated to be 0.98, which indicated a highly significant relationship between interlaminar shear strength and void content. Figure 16 shows the data plotted and also the least-squares regression line fitted to these data. The equation for this line showing the relationship between the two variables is

$$Y_{SH} = 13,550 - 724.7 X_V$$

where Y_{SH} and X_V are the interlaminar shear strength and the volume-percent void content, respectively.

The close fit of the regression line to the plotted data seems to confirm a linear inverse relationship between the two variables as was shown by Hand (2) for flat 2:1 orthogonal laminates. An examination of the data, particularly in the region of low void content (less than 1 vol-%) indicates, however, that perhaps a curve would fit the data better. A least squares regression analysis was performed

TABLE 3

Data for Glass-Filament-Wound NOL Rings Arranged to Show that the Interlaminar Shear Strength Increases as the Void Content Decreases*

Ring Number	Glass Content (wt-%)	Void Content† (vol-%)	Interlaminar Shear Strength (10 ³ psi)
9	—	5.20	9.85
30	—	5.00	9.92
10	—	4.50	10.55
8	83.9	4.20	10.67
32	—	3.60	11.00
12	—	3.50	11.03
11	83.7	3.40	10.58
15	82.9	2.40	11.46
29	—	2.18	11.87
14	84.8	1.60	12.71
Mc#7	—	1.60	12.30
23	—	1.10	13.06
27	—	0.70	12.77
24	85.2	0.64	13.17
25	—	0.37	12.93
JR-1	76.0	0.40	13.04
JR-4	75.8	0.18	13.54
JR-2	75.0	0.16	13.98

*Resin System, Epon 826(100)/MNA(85)/BDMA(1); Cure, 2 hr at 110°C (230°F), 2 hr at 140°C (284°F), and 2 hr at 175°C (347°F); Glass System, S-994 HTS.

†Determined by the point-count method.

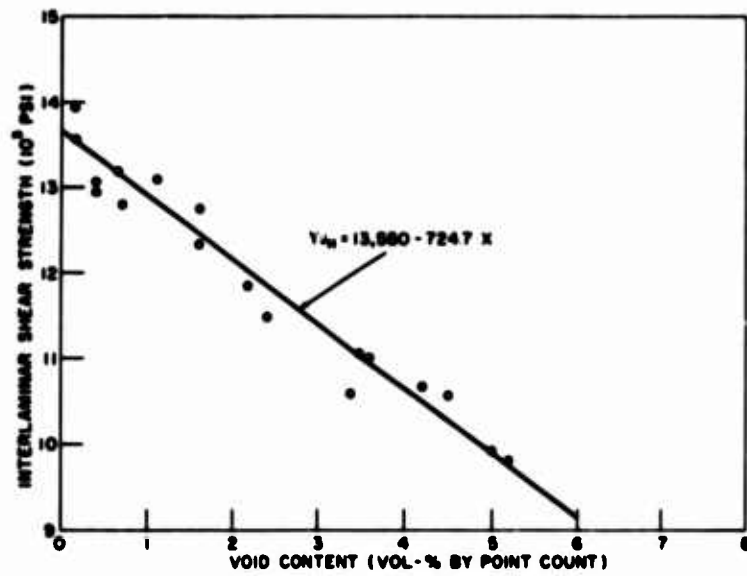


Fig. 16 - Graph showing the linear inverse relationship between the interlaminar shear strength and the void content of glass-filament-wound NOL rings

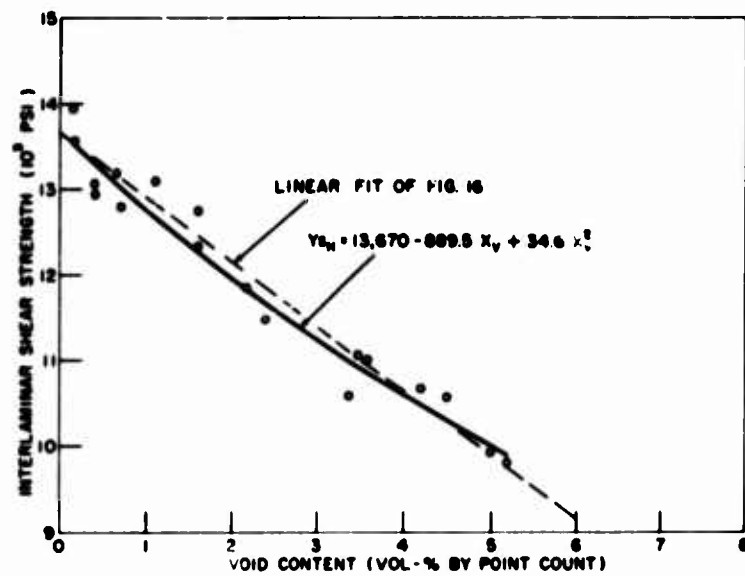


Fig. 17 - Graph showing second-order equation regression analysis curve fitted to interlaminar shear strength and void-content data

on the data in Table 3 to obtain the second-order equation

$$Y_{SH} = 13,670 - 889.5 X_V + 34.6 X_V^2$$

for the relationship between the two variables. The second-order regression curve fitted to the data (Fig. 17) also indicated a high degree of fit. The standard deviations calculated for the two equations were 270 and 260, respectively, indicating little significant difference between the fit of these equations to the data; hence the linear inverse relationship appears to adequately describe the correlation between the two variables. However, more data is needed in the void-content region below 1 vol-% to definitely establish the intercept at 0 vol-%. Such information would be useful in determining whether the gain in interlaminar shear strength would warrant further efforts in reducing the void content, particularly if elaborate modifications in the winding system are required.

Glass-content data were available for only eight of the rings. The calculated correlation coefficient r was 0.5, which indicated that the correlation between the interlaminar shear strength and the glass content was poor. However, since the calculation was based on limited data, this conclusion is only tentative. These analyses appear to establish the void content as the primary factor influencing the interlaminar shear strength of these structures and other variables such as glass content have only a second-order effect.

It may also be deduced from this analysis that the high degree of correlation between the void content and the interlaminar shear strength is indirect supporting evidence of the preciseness of the point-count method for the quantitative measurement of the void content of composite structures. Such close correlation would not be likely unless the method was reasonably precise.

CONCLUSIONS

A statistical point-count method adapted from petrographic modal analysis is believed to be a more precise, rapid, and versatile research method for void-content determinations in filament-wound composites than other techniques presently

being used, especially at low-void-content levels (<1 vol-%). Further study is needed to determine the accuracy of the method.

Filament-wound NOL rings with low void content (<1 vol-%) can be fabricated by a continuous single-strand winding process in which the resin is impregnated at reduced pressure with a vacuum applied only to the resin bath. More work is needed to determine if the vacuum process is feasible for multiple-strand fabrication of larger structures.

At least for the experiments performed on this project, working of the glass strand by means of guide rolls and vibration during resin impregnation, either at atmospheric or reduced pressure, is not as effective in decreasing the void content of glass-filament-wound NOL rings as is the vacuum resin impregnation technique alone.

A linear inverse relationship exists between interlaminar shear strength and the void content of filament-wound NOL rings. More data are needed to determine if this relationship is valid for values of void content less than 1 vol-%.

The void content of these structures is the primary factor influencing interlaminar shear strength, and other variables such as glass content appear to have only a second-order effect.

Numerous built-in flaws which may be potential stress concentrators and abrasive agents are present in the commercial glass yarn used in filament winding technology. These flaws are readily revealed by examination of the yarn under a light microscope.

The high degree of correlation between the interlaminar shear strength and void content derived from a statistical regression correlation analysis is indirect evidence that the point-count method for the quantitative measurement of void-content of composite structures has a relatively high degree of precision.

ACKNOWLEDGMENTS

The assistance and counsel of Mr. William Graner and Mr. John F. Freund of the Naval Ship Systems Command and Mr. Willard D. Bascom of this Laboratory are gratefully acknowledged.

REFERENCES

1. Paul, J.T., Jr., and Thomson, J.B., "The Importance of Voids in the Filament-Wound Structure," Proc. 20th Tech. Conf., SPI Reinforced Plastics Division, Section 12-C, Feb. 1965
2. Hand, W., "Quality Control of Filament Wound Materials for Deep Submergence Vessels," Proc. 20th Technical Conference, SPI Reinforced Plastics Division, Section 1-E, Feb. 1965
3. Fried, N., "The Response of Orthogonal Filament Wound Materials to Compressive Stress," Proc. 20th Tech. Conf., SPI Reinforced Plastics Division, Section 1-C, Feb. 1965
4. Bascom, W.D., "Some Surface Chemical Aspects of Glass-Resin Composites, Part 1—Wetting Behavior of Epoxy Resins on Glass Filaments," NRL Report 6140, Aug. 10, 1964; "Part 2—The Origin and Removal of Microvoids in Filament-Wound Composites," NRL Report 6268, May 24, 1965; Proc. 20th Tech. Conf., SPI Reinforced Plastics Division, Section 15-B, Feb. 1965
5. Nielsen, L.E., "Mechanical Properties of Polymers," New York:Reinhold, 1962, p. 232
6. McNeil, D.W., and Bennett, B., *Mod. Plastics* **42**(No. 4): 143 (1964)
7. Chayes, F., "Petrographic Modal Analysis," New York: Wiley, 1956
8. Hilliard, J.E., and Cahn, J.W., *Trans. AIME* **221**:344-352 (1961)
9. Howard, R.T., and Cohen, M., *Trans. AIME*, **172**:413 (1947)
10. Sands, A.G., Clark, R.C., and Kohn, E.J., "Microparticle and Fiber Reinforcement of Epoxy Resins," NRL Report 6403, Aug. 26, 1966
11. "Evaluation of Low Void Content Glass-Filament-Wound NOL Rings Fabricated by McClean-Anderson, Inc.," NRL letter report to Chief, BuShips (Code 634C), Ser. 965, February 7, 1965, BuShips Project SR 007-03-04-1008

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE MICROVOIDS IN GLASS-FILAMENT-WOUND STRUCTURES: THEIR MEASUREMENT, MINIMIZATION, AND CORRELATION WITH INTERLAMINAR SHEAR STRENGTH			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) An interim report on a continuing problem.			
5. AUTHOR(S) (First name, middle initial, last name) A. G. Sands, R. C. Clark, and E. J. Kohn			
6. REPORT DATE March 31, 1967		7a. TOTAL NO. OF PAGES 24	7b. NO. OF REFS 11
8a. CONTRACT OR GRANT NO. NRL Problem C03-19		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6498	
b. PROJECT NO. SF 020-04-01-1068		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.			
d.			
10. DISTRIBUTION STATEMENT Distribution of this document is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Naval Ship Systems Command), Washington, D.C. 20360	
13. ABSTRACT Microvoids in glass-filament-wound composites are being investigated to develop a reliable research method for the quantitative measurement of void content in these structures, to develop techniques for minimizing the number of microvoids in the composites, and to determine how significantly voids affect the structural integrity of the finished composite. The NOL glass-filament-wound ring is being used as a model. A statistical point-count method adapted from petrographic modal analysis has been studied as a quantitative means of measuring void content and tentatively appears to be a more precise, rapid, and versatile method than other techniques presently being used, especially at low-void-content levels (<1 vol-%). Low-void-content (<1 vol-%) filament-wound NOL rings have been fabricated by a continuous single-strand-winding process and resin impregnation at reduced pressure with the vacuum applied only to the resin bath. Working of the strand during the resin impregnation step by various configurations of guide rolls and strand vibrating devices either at atmospheric or reduced pressure was relatively ineffective in decreasing void content as compared with vacuum resin impregnation alone. Regression correlation analysis studies have shown that a linear inverse relationship exists between the interlaminar shear strength and the void content of NOL rings and that void content is the primary factor influencing interlaminar shear strength. The high degree of correlation between interlaminar shear strength and void content derived from the statistical regression correlation analysis is indirect supporting evidence that the point-count method for the quantitative measurement of the void content of composite structures has a relatively high degree of precision.			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Epoxy plastics Glass fibers Filament winding Binders NOL rings Manufacturing methods Compressive properties Tensile properties Interlaminar shear strength Defects (materials) Techniques for minimizing voids Voids Microvoids Measurement Statistical analysis Microscopic volume-fraction analysis						