NRL Report 7246

Fatigue Behavior of Glass-Filament-Wound Epoxy Composites in Water

J. B. Romans, A. G. Sands, and J. E. Cowling

Organic Chemistry Branch
Chemistry Division

April 5, 1971

NAVAL RESEARCH LABORATORY
Washington, D.C.

[redacted]

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

UNCLASSIFIED

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
MATERIALS	2
TEST METHODS	4
Fatigue Test	4
Preparation of Specimens	6
Determination of Glass Content, Void Content, and Interlaminar Shear Strength	8
FACTORS FOUND TO INFLUENCE THE FATIGUE BEHAVIOR OF GLASS-FIBER EPOXY COMPOSITES	8
Environment: Air Versus Water	8
Dynamic Versus Static Stress	10
Maximum Fiber Stress Imposed on the NOL Ring	11
Effect of Curing Schedule	11
Effect of Additives in Altering Properties of the Matrix	12
Effect of Curing Agent	13
Inherently Water-Resistant Epoxies	13
DISCUSSION	17
CONCLUSIONS	18
ACKNOWLEDGMENTS	19
REFERENCES	19

ABSTRACT

The significance of matrix compositions has been studied in relation to the fatigue characteristics of glass-filament-wound reinforced plastics. Evidence indicates that water, as compared with air, severely limits the dynamic fatigue life of glass-reinforced epoxy plastics. It is suggested that a relationship may exist between matrix degradation and the time-dependent response of the composite material to dynamic stresses. A new, very-water-resistant epoxy resin is shown to increase the reliability of glass-fiber-reinforced plastic by 200 to 300% in comparison with an equivalent state-of-the-art composition exposed to the same type of stress and environmental conditions.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

NRL Problem C03-19
Project SF 51-544-102-12432

Manuscript submitted January 8, 1971.

UNCLASSIFIED

FATIGUE BEHAVIOR OF GLASS-FILAMENT-WOUND EPOXY COMPOSITES IN WATER

INTRODUCTION

For a number of years NRL has been engaged in a research program directed toward developing high-performance composites for Navy-wide use. The glass-reinforced plastics used in Polaris motor cases demonstrated the usefulness of these materials where a high strength-to-weight structure was required. A more advanced objective is the use of reinforced plastics in undersea structures, even including, in the more distant future, the pressure hulls of deep submergence craft.

Although glass-fiber-reinforced plastics can fulfill many very-high-performance requirements, their true potential as engineering materials is not being realized because designers and users lack confidence in their reliability. Many researchers have reported that water degrades the strength of glass-fiber-reinforced plastics, but very few have provided information that quantitatively relates degradation to composition as a rate process. Even less information is available on the effectiveness of corrective measures that might be undertaken to counteract the adverse effects of water. The authors have long held that a deep-ocean structure should have two strong lines of defense against water. The first line of defense should be a buoyant, highly impermeable protective coating, perhaps of massive thickness, such as obtainable with polypropylene. The second line of defense ought to be a resinous matrix of intrinsically high resistance to all forms of hydrolytic attack. Therefore, much of NRL's efforts to advance the technology of reinforced plastics has sought (a) to develop resins of improved strength and water resistance (1-5), and (b) to determine the effects of environment and fatigue on the reliability of composite materials using these improved resins. Methods of increasing quality assurance also have been studied, especially methods for producing composites containing fewer voids (6-8).

Although glass-reinforced plastics are not subject to corrosion as are metals, very little is known about their behavior when they are exposed to water under the high pressures of great sea depths and subjected to the dynamic strains that mobile undersea craft must withstand. It is to be expected that the optimum performance of a glass-reinforced plastic deep-ocean structure will depend on total integrity of the composite material, involving all properties intrinsic to the resin and reinforcement, in combination with the bond between the resin and the reinforcement. The durability of the glass-to-resin bond is believed to be a major determinant of the ability of the composite to withstand repeated strain under water. Hence, the glass is given a silane-type "finish," which acts as a coupling agent to promote adhesion between resin and reinforcement. This finish and the entire interfacial zone have been the subject of much research (9,10).

Tensile stress applied to a glass-reinforced plastic will produce craze cracking when the maximum strain capability of the resin is exceeded (11,12a). When this occurs in a dry environment, the strength of the composite may be only slightly impaired. However, the strength of a glass-reinforced plastic is greatly reduced when moisture enters these cracks, from which attack then occurs not only on the glass-resin bond but also on the glass itself. Under repeated flexing, adhesion between the glass and resin fails, breakage of the reinforcement occurs, and the integrity of the structure is destroyed. Thus, a

glass-reinforced plastic structure would be expected to deteriorate more rapidly under water, if it is repeatedly subjected to high stresses, than in dry (or low humidity) air. Evidence of this has been seen repeatedly in NRL's investigations.

As with metals, study of the fatigue characteristics of glass-reinforced plastics is time consuming; many experiments must be conducted to obtain comprehensive data. Variables, such as glass content and void content are not always easy to control and can adversely affect fatigue life (13). However, if glass-reinforced plastics are to be used in the primary structure of deep submergence craft, an exhaustive study must be made of material reliability, and effective measures must be developed to overcome their susceptibility to the deteriorating effects of water.

This report has two purposes: (a) to shed more light on the relationship between material composition and material reliability and (b) to point the way to improving the "second line of defense" against water, that is, to develop more water-stable resins than presently are used in structural glass-fiber composites. This relationship is being studied on the basis of damage to the material by the environment (primarily water) and high dynamic stresses. Because of the complex nature of composites, it is almost impossible to eliminate some other factors affecting material reliability. Mainly, these other factors correlate with difficulties in quality control, especially with problems in fabrication. These factors are noted and discussed where they have significantly determined the outcome of the experiments.

MATERIALS

In contrast to much other work, a precept of this investigation has been the study of glass-fiber-reinforced plastics as materials rather than structures. The variables of main interest are the numerous types of resinous matrices and the proportions in which they can be used with the glass-fiber reinforcement. Only one type of glass—type S—is used in the highest-strength glass-reinforced plastics (GRP), and in NRL's studies no discernible difference has been detected in the quality of composites made with type S glass fiber from two sources—the Owens-Corning Fiberglas Corporation and the Ferro Corporation. Therefore, glass fiber is a variable in this investigation only with respect to its volume-proportion in the composite. The composition of the total composite, by volume, is always % glass + % resin + % voids = 100%.

Type S glass fiber is composed of 65% SiO_2, 25% Al_2O_3, and 10% MgO (12b). It is normally supplied in continuous strands of 204 filaments each. That supplied by the Owens-Corning Fiberglas Corporation is designated as S-994 with an HTS finish; that obtained from the Ferro Corporation is designated as S-1014 with an S-24 "nonaging" finish. At 75°F S-994 glass is reported to have a virgin fiber tensile strength of about 700,000 psi and Young's modulus of 12.4×10^6 psi (14). Corresponding data on the S-1014 glass is a 656,000-psi tensile strength and Young's modulus of 12.6×10^6 psi (14). The glass is refrigerated at 14°F from the time it is received until it is placed on the winding machine for use.

Epoxy resins based on the diglycidylether of bisphenol A are widely used in filament-wound reinforced plastics. A typical epoxy resin of this type is Epon 826, a product of the Shell Chemical Company. This epoxy, cured with nadic methyl anhydride (NMA) and catalyzed with benzyldimethylamine (BDMA), has been used as a "reference" matrix throughout this program.

A broad range of other epoxy resins has been evaluated in NOL rings against the reference composition. Specific information on the composition of all epoxy resins and curing agents is given in Tables 1 and 2, as well as in subsequent sections describing individual experiments. The chemistry involved in the reactions of the various resins

UNCLASSIFIED

Table 1
Epoxy Resins

Resin Designation	Composition	Source
Epon 826	Diglycidyl ether of bisphenol A	Shell Chemical Company
ERL 2256	Diglycidyl ether of bisphenol A, 62.5%; 2,3-epoxycyclopentyl ether, 37.5%	Union Carbide Corporation
Resorcinol epoxy	Resorcinol diglycidyl ether	Koppers, Inc.
ERLA 0400	2,3-epoxycyclopentyl ether	Union Carbide Corporation
Velsicol DGEHQ	Chlorinated epoxy resin (45% chlorine)	Velsicol Chemical Corporation
ERX-67	N,N-bis(2,3-epoxypropyl)tribromoaniline	Shell Chemical Company
Epon 1031*	Polyglycidyl ether of tetraphenylene ethane	Shell Chemical Company
Epon 828*	Diglycidyl ether of bisphenol A	Shell Chemical Company
ERLA 4617	Copolymer of bis-epoxycyclopentylether and a polyol	Union Carbide Corporation

*Resin constituents of 5868R prepreg, a product of the Chicago Printed String Co.

Table 2
Curing Agents

Designation	Composition	Source
Nadic methyl anhydride (NMA)	Methylbicyclo(2,2,1)heptane-2,3-dicarboxylic anhydride isomers	Allied Chemical Corporation
BDMA	Benzyldimethylamine (used as accelerator)	Eastman Organic Chemical Div. of Eastman Kodak Company
HHPA	Hexahydrophthalic anhydride	Allied Chemical Corporation
MOCA	4,4' -Methylene-bis-(2-chloroaniline)	E. I. duPont deNemours & Co., Inc.
MPDA	meta-Phenylenediamine	Miller-Stephenson Chemical Co., Inc.
MABA	meta-Aminobenzylamine	Dr. J. R. Griffith, NRL
Bakelite ZZL-0820	Eutectic blend of aromatic amines	Union Carbide Corporation
MDA	Methylene dianiline	Curing agent used in NOL rings supplied by Union Carbide Corp.

and curing agents may be found in any standard reference on epoxy resins (15) and therefore is not included in this report. While the major emphasis of this work has been on epoxy resins, per se, some attention has been given to the possibility of using additives that might contribute beneficial chemical and physical properties to the composite material. Identification and specific information concerning these additives are given in Table 3.

Manufacturing methods can have a pronounced effect on composite material quality. In this particular research, it was not intended that a systematic study be made of processing factors, i.e., fiber tension in winding, faulty impregnation (voids), curing schedule, etc. Nevertheless, the significance of these factors has inevitably come under observation, particularly in those instances where processing factors appear to have appreciably determined the outcome of an experiment. Poor quality control in making the test specimens can result in an inferiority of the specimen's quality which will overshadow any worthwhile contribution the material constituents can make to improve the fatigue and environmental resistance of the composite.

Table 3
Additives

Designation	Composition	Source
Silicone	SF-96 Silicone oil; viscosity: 1000 cs at 77°F	General Electric Company
A-1100	γ-Aminopropyltriethoxysilane	Union Carbide Corporation
Syl-Kem 90	1,3-bis 3(2,3-epoxypropoxy)propyl-tetra-methoxy siloxane	Dow-Corning Corporation
Fluorosilicone	FS 1265 Fluorosilicone; viscosity: 250 cs at 77°F	Dow-Corning Corporation
Aroclor 1254	Chlorinated biphenyl	Monsanto Chemical Company

TEST METHODS

Fatigue Test

Studies by Fried, Kaminetsky, and Silvergleit (16) showed that glass-resin composites rapidly deteriorate under stress, both in shear and compression when they are immersed in water, and that the loss in strength is considerably greater if the stress is applied and removed repeatedly. Abbott, Cornish, and Cole (17) have shown that it is best to employ a low-rate cyclic stress on composite specimens in relating their dynamic fatigue characteristics to deep submergence objectives. Prosen et al. (18a) at the Naval Ordnance Laboratory studied the fatigue characteristics of glass-reinforced plastics by cutting sections from NOL rings and fatiguing them in a device that applied a combination of torsion and flexural stresses. Other researchers, including the Union Carbide Corporation (19), have used high cyclic rates in flexural fatigue tests on flat laminate specimens. Obviously, there is no agreement on specific conditions for studying the fatigue of fiber-reinforced plastics. Most researchers have devised methods which they feel satisfy their particular objectives.

For this investigation it was decided that a low-cyclic-rate flexural test could provide reliable information on the significance of material composition in relation to fatigue in the presence of an adverse environment such as water. The simplest, most reproducible specimen for such an investigation is the NOL ring which is widely used to study fiber-reinforced plastics (20). The fatigue of such a specimen can be easily sensed by monitoring its "compliance*" at a fixed amount of strain in repetitive cycling. A low cycling rate eliminates the problem of internal temperature rise which will occur if the cyclic rate is rapid (18a).

Specifically, the test selected involved compressing NOL rings in 24 seconds to ellipse-like ovals between two parallel plates to a predetermined maximum strain. This strain was held for 1 minute, released to zero strain in 3 seconds, held at zero strain for 3 seconds, and then the cycle was repeated. The load required to compress a ring progressively decreases with the specimen fatigue. The test is quite sensitive in detecting damage. Usually this test was concluded when the load required to compress a ring had dropped 20% from that required on the first cycle.

The parallel plate assembly (Fig. 1) was designed to hold up to 39 rings. When tests were made in water, the entire assembly was placed in a stainless-steel tank filled with

*Disposition to yield; in this case, compliance refers to a decrease in effective modulus.

UNCLASSIFIED

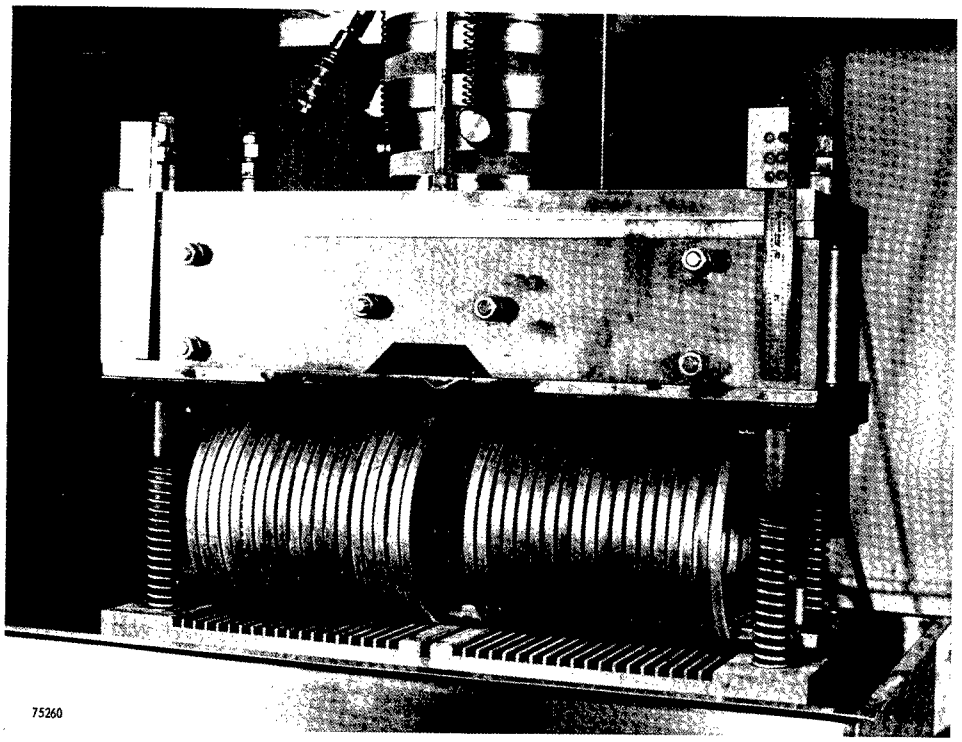


Fig. 1 - Parallel plate assembly for fatigue testing of NOL rings

distilled water, which was changed at the conclusion of each test. Salt water was not used because it is potentially corrosive to the testing machinery and because research elsewhere (21-23) has shown fresh water to be as severe as salt water, or slightly more so.

The machine used to compress the parallel plate assembly was a closed-loop Electro-Hydraulic Materials Testing System made by the MTS Systems Corporation, Minneapolis, Minnesota. Loads imposed on the rings were measured either with remote-indicating electronic load cells made by W. C. Dillon and Company, Inc., Van Nuys, California, or with an Instron Tester made by the Instron Engineering Corporation, Canton, Mass. In the latter case the fatigue test had to be interrupted briefly for short periods to make load measurements with the Instron equipment.

From the geometry of a diametrically compressed NOL ring it is readily seen that the maximum fiber stress in tension is on the outer circumferential surface of the ring at points 90° from the applied load (24). Maximum stress in compression occurs on the inner circumferential surface at corresponding points. The maximum fiber stress in tension was determined at point A, shown in Fig. 2, with SR-4 strain gages made by BLH Electronics, Inc., Waltham, Mass. Measurements made on many rings showed that the maximum fiber stress in tension was roughly proportional to the degree of bending of the NOL ring and did not vary significantly over the range of GRP compositions used in this study. The maximum tensile fiber stress on the inside surface was measured in the same way by placing the strain gage at position B shown in Fig. 2. Figure 2 shows that the stress and elongation on the inner surface of an NOL ring reaches a plateau at about 2.5 inches diametrical compression; further compression has little additional effect on the stress at point B.

This method of fatigue testing was used over a broad range of stress levels on NOL rings composed of 56 to 58 vol-% glass in the epoxy resin Epon 826/NMA/BDMA.

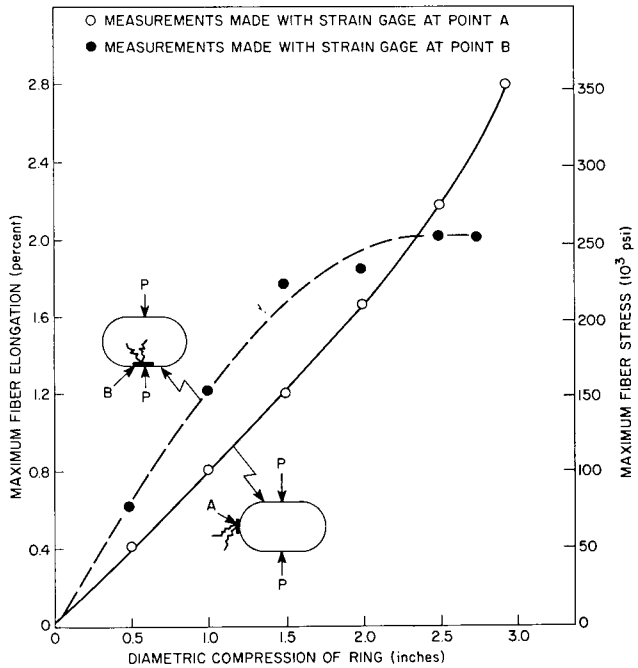


Fig. 2 - Evaluation of stress and strain in NOL rings under diametric compression. The resin system being considered was Epon 826/NMA/BDMA and the glass was Ferro S-1014 with a modulus of 12.3×10^6 psi. The load was applied at point P and measured at points A and B with the strain gages.

However, most experimental GRP compositions were "screened" at a maximum fiber stress of 280,000 psi (2.2% fiber strain), which was produced by compressing the rings 2.53 inches to a short axis diameter of 3.47 inches. This test severity was chosen by considering four factors: (a) the minimum practical proportion of glass is likely to be 56 to 58 vol-% in most structural applications because of the lack of stiffness associated with lower glass contents, (b) the fatigue life (approximately 5000 cycles for the reference composition) is usably high, though less than sought, (c) the elongation (strain) of the reference matrix (Epon 826/NMA/BDMA) is about 10% less than its reported ultimate, i.e., 2.2% versus 2.4% (15) and (d) experience has shown that fatigue tests run in water at 240,000 psi maximum tensile stress required excessively long test periods while tests run at 320,000 psi resulted in very short test periods or excessive ring breakage. The fatigue test at 280,000 psi maximum fiber stress (±10,000) is referred to as "standard" throughout this report. Where other test conditions have been used, they are described specifically in each instance.

Prior to undergoing fatigue testing, all rings were "conditioned" by several days of exposure to 50% R.H. air at 72°F. Tests in air were made under these conditions. Tests in water were made at the same temperature, with the rings submerged.

Preparation of Specimens

As previously indicated, NOL rings were used in the fatigue studies. These are glass-reinforced filament-wound rings which are 5.75 in. I.D. by 6.00 in. O.D. by 0.250 in.

UNCLASSIFIED

wide. These rings are essentially unidirectionally reinforced materials. They are relatively uncomplicated structures and are equivalent to the type C test specimen of ASTM Recommended Practice D 2291-67 (20).

In most instances, the NOL rings were made by impregnating the glass strands while drawing them through a resin bath, then winding the impregnated strands on Teflon-coated steel ring molds. Both single-strand laboratory winding equipment and a commercial-type multistrand machine were used, the choice depending mainly on the quantity of material available and number of specimens required. The multistrand machine was made by Lamtex Industries, Inc., Farmingdale, N.Y. With this machine, 30 to 40 glass strands can be wound at one time. The void content of rings typical of the wet-winding art when using 30 to 40 "ends" may average from 3 to 5 vol-%.

Rings containing less than 1 vol-% voids were made with the Epon 826/NMA/BDMA matrix by winding with only 12 strands, spaced separately, and passed around a grooved pulley located in the bottom of the resin bath. The combined tension at the mandrel on all 12 strands was maintained between 300 and 400 grams at a winding speed of about 12 feet per minute. The temperature of the water-heated resin bath was maintained between 135° and 140°F to hold the resin viscosity within a range that permitted good strand impregnation. All winding was done in an air-conditioned room at approximately 50% relative humidity and 72°F. However, it was impossible to obtain a void content below 1% with all resin systems, often because of their high viscosity or short pot life at reasonable processing temperatures, or both. A limited number of rings, containing in some instances as few as 0.1 vol-% voids, was made by winding 30 strands of glass directly onto the ring mold and then impregnating in situ by a vacuum process (7). A few rings were wound with commercial, preimpregnated roving (prepreg).

Experience in this study has shown that a value of 2 vol-% voids is a practical objective for quality control in the fabrication of most GRP compositions. Voids within the range of 1 to 3% have not obscured the significance of the resin as a vital determinant of the fatigue and environmental resistance of the composite material.

After curing, all rings were brought to correct thickness (±0.002 inch) by grinding the outer circumferential surface. A water-soluble grinding aid was used. Other dimensions (width and diameter) were controlled by the mandrel on which the rings were wound.

Reference 12c reported a decrease in properties of unidirectionally reinforced composites when the glass content is very high. Since glass content is an important compositional variable, its effect on ring fatigue was studied over the range of approximately 50 to 73 vol-% in the "reference" matrix (Epon 826/NMA/BDMA) and one experimental resin (ERX-67). Otherwise, an effort was made to control glass content within 58 ± 2 vol-%, but this was not always achieved because of the poor working properties of some materials.

A large number of experiments were conducted on NOL rings made with the "reference" matrix, Shell Epon 826 resin cured with nadic methyl anhydride and benzyldimethylamine as the accelerator (Epon 826 - 100 parts, NMA - 85 parts, and BDMA - 1 part, by weight). In preparing the mixture, the resin was warmed in a 140°F water bath and dissolved air was removed with a Rimco rotating evaporator at 2 mm Hg. The NMA was added to the resin, which then was warmed, mixed, and reevacuated. Finally, the BDMA accelerator was added and any remaining bubbles removed under vacuum before the mixture was put in the water-heated resin pot on the winding machine.

After winding, rings made with the resin system were cured in an oven on the following schedule: 2 hours at 225°F, 2 hours at 275°F, and 2 hours at 330°F. They were allowed to remain in the hot oven after it was turned off until the ring mold cooled to room temperature, i.e., about 16 hours.

Rings always were prepared in batches of eight except in a few instances when the quantity of one of the experimental materials was limited. Fatigue evaluation was made on five rings of each batch; one was used for destructive tests, e.g., glass content, void content, interlaminar shear strength, and the remaining two were set aside for future reference, if needed. Frequently the same composition was rerun in a number of batches to increase the reliability of the data. Quality control was found to be a continuing problem necessitating the collection of data on many rings to give high confidence in the result. Every new experimental composition had its own unique rheological properties and this, of course, complicated the problem of quality control. Generally, the coefficient of variation in data, following these procedures, was within ±16%. Variations in excess of 16% always could be attributed to poor working properties of the materials and consequent deficiencies in quality control.

Determination of Glass Content, Void Content, and Interlaminar Shear Strength

The weight-percent glass of NOL rings was obtained by burning off the resin from weighed segments of rings. A rather close approximation of the glass content of a whole ring can be obtained by measuring the load the ring will support at a given amount of deflection (i.e., its effective modulus) and comparing this relationship with data obtained on rings made with the same resin and containing known amounts of glass. Resonant frequency measurements also can be used if an appropriate calibration curve exists. Both of these techniques were used to select matched sets of rings for fatigue studies.

The void content of the test rings was determined by using a point count method from a petrographic modal analysis technique (8,25). Thin sections were cut from the rings and the number of voids counted in a given area with the aid of a microscope and grid system. The void content was obtained as volume-percent. This method is simple and fast but does destroy the ring. However, the method can be used on undamaged parts of rings after completion of the fatigue test.

Interlaminar shear strength data were obtained by the horizontal short-beam method in accordance with ASTM Recommended Practice D 2344-67 (26).

FACTORS FOUND TO INFLUENCE THE FATIGUE BEHAVIOR OF GLASS-FIBER EPOXY COMPOSITES

Environment: Air Versus Water

Table 4 gives the cyclic fatigue life *in air* of a series of 14 NOL rings made with the Epon 826/NMA/BDMA resin system. For this particular set of experiments, the rings were subjected to diametrical displacements varying from 2.53 to 2.77 inches (approximately 280,000 psi to 330,000 psi maximum outer fiber stress). Despite the severity of this test and the rather wide range in void content, none of the rings failed before 10,000 cycles were reached. The compliance for each series varied from 3.5 to 8.7%. The average compliance for all 14 rings was approximately 6% at 10,000 cycles.

The adverse effect of water on the cyclic fatigue life of rings made with the same materials and containing about the same amount of glass is clearly seen by comparing the data in Table 5 with those in Table 4. At 280,000 psi maximum fiber stress the average fatigue life of 28 rings in distilled water was a fraction of that of rings tested in air. The scatter of the data is quite large, though not unusual for dynamic fatigue tests of composite materials (18b). The average deviation was about 900 cycles or 18% variation from the mean.

UNCLASSIFIED

Table 4
Physical Properties and Cyclic Fatigue Life in Air of NOL Rings
Made With the Epon 826/NMA/BDMA Resin System

Glass* (vol-%)	Voids* (vol-%)	Interlaminar Shear Strength* (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Average Drop in Load, After 10,000 Cycles (%)
54.9†	5.0	12,000	330,000	2	7.8
57.6†	5.8	11,000	315,000	5	3.5
58.9†	0.2	13,600	300,000	2	8.7
56.3‡	0.4	13,600	280,000	5	7.4

*Value from ring of same lot.
†Owens-Corning S-994 glass.
‡Ferro S-1014 glass.

Table 5
Physical Properties and Cyclic Fatigue Life in Water of NOL Rings
Made With the Epon 826/NMA/BDMA Resin System

Glass*† (vol-%)	Voids* (vol-%)	Interlaminar Shear Strength* (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Average Life (cycles)
57.4	0.8	13,400	280,000	28	5,400
58.3	2.4	13,200	320,000	6	3,100

*Value from ring of same lot.
†Ferro S-1014 glass.

Figure 3 graphically illustrates the compliance of two rings typical of those listed in Tables 4 and 5, one tested for 14,000 cycles in air and the other for 6000 cycles in water. The appearance of these same rings under diametrical compression after the tests were concluded is shown in Fig. 4. Damage to the rings is visible as "brooming" of broken glass fibers in the areas of high fiber stress, the same locations where strain gages were placed on the rings shown in Fig. 2. It is also seen that the brooming effect is much greater on ring C, which was fatigued in water, than on ring B, which was fatigued in air.

The physical mechanism of fatigue failure of rings in water was studied by using a microscope. It was observed that failure had been initiated on the outermost surfaces at the points of maximum fiber stress. First, minute cracks occurred in the resin; then the resin-glass bond was attacked, releasing the outermost fibers from the matrix, occasionally before they broke. With the rings made with the Epon 826/NMA/BDMA resin system, the resin seemed to crumble away. Since it has been established that some degree of failure (cohesive, adhesive, or both) occurs when a glass-fiber reinforced resin is flexed, even during the first cycle (27), this phenomenon obviously provides initial pathways for the entrance of water into the composite. (Other researchers have shown that the penetration of moisture into filament-wound cylinders under hydrostatic pressure depends directly on the extent of crazing of the resin in the structure (28).) As flexing is continued, cracks become larger and more numerous until water reaches the resin-glass bond from which point the water spreads very rapidly along the surface of the

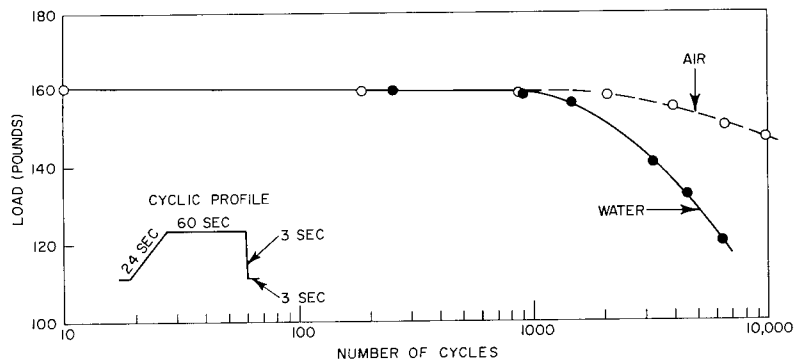
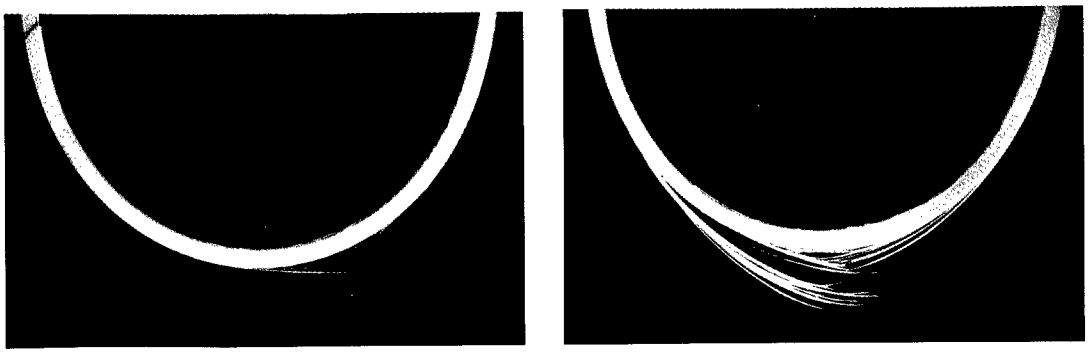


Fig. 3 - Effect of environment on the cyclic fatigue life of typical NOL rings. The resin system was Epon 826/NMA/BDMA, and the glass was Ferro S-1014.



(B) (C)

Fig. 4 - Effect of cyclic fatigue on typical NOL rings after 14,000 cycles in air (B) and 6000 cycles in water (C)

glass (29). When this stage is reached, the glass fibers come under chemical attack by the water, weakening them until they break under stress. Since the fibers are already loosened from the resin, the broken ends spring out causing the brooming effect seen in Fig. 4. It is seen, then, that the loads needed to produce a given strain on the rings decrease because damage reduces the effective cross-sectional areas in the highly stressed sections of the rings.

Dynamic Versus Static Stress

To prove the point that it is repeated flexing that plays a major role in the fatigue of NOL rings in water, four rings of the same composition as those studied previously were diametrically compressed by means of screw clamps and stored in distilled water. As shown in Table 6, it required 14 to 16 months of exposure to the water under constant strain before the compliance of these rings averaged 19%. This is compared to some 5 days of flexing under water for similar rings to fail in cyclic fatigue (Table 5). Similar results have been obtained by Fried and coworkers (16) in somewhat related studies.

UNCLASSIFIED

Table 6
Physical Properties and Static Fatigue Life in Water of NOL Rings Made With the Epon 826/NMA/BDMA Resin System

Glass* (vol-%)	Voids* (vol-%)	Interlaminar Shear Strength* (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Compliance (%)			
					3 mo	6 mo	14 mo	16 mo
60	2.0	12,500	310,000	4	2.0	5.6	18	19

*Value from ring of same lot.

Maximum Fiber Stress Imposed on the NOL Ring

Obviously fatigue life will be affected by stress employed in the fatigue tests. This is shown graphically in Fig. 5 by the results of tests in water on 51 rings made with the Epon 826/NMA/BDMA resin system. Here the fatigue life obtained is related to the maximum outer fiber stress. The decrease in fatigue life with rising maximum outer fiber stress is pronounced and quite linear in the restricted range of stresses used in this study.

Effect of Curing Schedule

Limited studies were made to determine if the final stage of the curing schedule (2 hours at 330°F) used for rings made with the Epon 826/NMA/BDMA resin system was

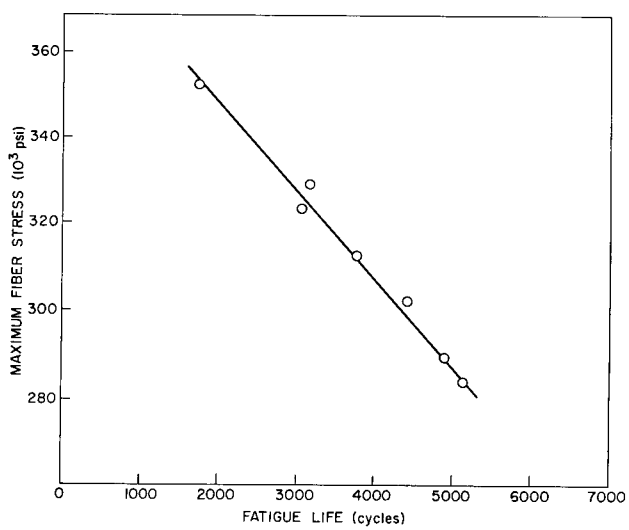


Fig. 5 - Effect of maximum outer fiber stress in NOL rings on the cyclic fatigue life in water. The resin system was Epon 826/NMA/BDMA, the glass content varied between 56 and 58 vol-%, and the average void content was 1.4 vol-%.

adequate. Extending the final curing stage to 16 hours at 330°F on a series of six rings resulted in an average cyclic fatigue life in water of 5100 cycles, essentially the same as that obtained after 2 hours at 330°F. However, a postcure of 8 hours at 400°F resulted in a considerably shorter fatigue life.

Effect of Additives in Altering Properties of the Matrix

It was obvious that there were at least two prominent deficiencies in the matrix, which, if overcome, might lead to considerably improved fatigue life of the resulting glass-fiber composite. Earlier work by the authors had shown that it is possible to extend the cyclic fatigue life of NOL rings in water by protecting them with a "waterproof" coating, but such a method has practical limitations when applied to complicated structures. It is much more desirable that the composite be inherently water resistant. The current work showed that cracking and crumbling of the resin led to early water penetration and fatigue failure of the composite. Obviously, a pressing need exists for inherently "waterproof" and tougher matrices.

Reduction of the wettability of the composite was sought through the use of silicone-type materials which are noted for their hydrophobic characteristics (30). The results of these experiments are shown in Table 7. Although the data are limited, it would appear that no significant improvement in fatigue life resulted from adding silicone-type materials to the resin. The average life of ten rings containing 1% of these additives was 5700 cycles compared with 5400 cycles obtained with untreated rings. Further, when the silicone content was increased approximately 10 times, the fatigue life was not improved.

Table 7
The Effect of Additives on the Physical Properties and Cyclic Fatigue Life in Water of NOL Rings Made With the Epon 826/NMA/BDMA Resin System

Additive	Glass*† (vol-%)	Voids* (vol-%)	Interlaminar Shear Strength* (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Range in Cycles to Failure	Average Life (cycles)
1 phr‡ Silicone§ 1/4 phr A-1100	54.1	1.2	12,600	280,000	3	4200-8000	5800
1 phr Syl-Kem 90	60.1	0.3	13,600	280,000	5	4800-6200	5500
1 phr Fluorosilicone¶	56.2	1.0	13,200	280,000	2	5800-6600	6200
10 phr Aroclor 1254	58.7	0.4	13,000	280,000	11	5300-8200	6700

*Value from ring of same lot.
†Ferro S-1014 glass.
‡Phr = parts per hundred parts of resin by weight.
§General Electric SF-96 silicone oil.
¶Dow-Corning FS 1265 fluorosilicone.

The cyclic fatigue life in distilled water was noticeably improved (26%) by adding Aroclor 1254, a flexibilizer often used in plastics (31). A series of 11 rings containing this material was fatigued under the same conditions as those containing the silicones. Table 7 also contains data on these rings. The average fatigue life was 6700 cycles with a mean deviation of about 800 cycles.

These data on Aroclor 1254 describe the state of research using this material in this project as of July 1, 1970. On August 30, 1970, the Monsanto Chemical Company stopped producing Aroclor 1254 and other polychlorinated biphenyls for use in coatings, plastics, and adhesives. Monsanto took this action when it was discovered that these materials, which are very stable and slightly toxic, might cause cumulative long-term harm to the natural environment.

UNCLASSIFIED

This event negates a considerable part of NRL's plans to investigate highly water-resistant "flexibilizers" for epoxy resins and relegates the results of experiments with Aroclor 1254 to academic interest only. This turn of events accentuates the importance of developing epoxy resins of intrinsically high water stability and environmental acceptability.

Effect of Curing Agent

Since the aromatic amines have been used extensively as curing agents for the diglycidyl ether of bisphenol A, fatigue studies were made with rings containing Epon 826 cured with meta-phenylenediamine (MPDA) and with meta-aminobenzylamine (MABA) (3). These curing agents react much more rapidly with Epon 826 (and other typical glycidyl ethers of bisphenol A) than do the anhydride curing agents. Consequently, the useful pot life of most amine-epoxy resin systems is comparatively short. To retard the reaction rate of the amine-epoxy filament-winding resins, the temperature of the resin bath must be some 15° to 20°F lower than that used with the "standard" (i.e., anhydride-epoxy) resin system. Under these conditions the viscosity of the resin mixture is high, causing poor impregnation (high proportion of voids in the composite). If the temperature is increased to lower the viscosity, the benefit is very temporary because the reaction progresses rapidly, causing the viscosity to rise. The reaction soon becomes exothermic and processing must cease. The rings wound with MPDA and MABA had void contents of over 7 vol-% and interlaminar shear strengths of only 8500 psi.

Five each of the MPDA and MABA-cured rings were subjected to cyclic fatigue in water at an outer fiber stress of 320,000 psi. All 10 rings failed before 1000 cycles had been reached (Table 8). A series of six rings made with the Epon 826/NMA/BDMA resin system, subjected to cyclic fatigue at the same high stress level, sustained 3100 cycles before failing. It is possible that the very low interlaminar shear strength of the MPDA and MABA-cured rings was responsible for their poor performance. At the lower stress of 280,000 psi, the MPDA-cured system had an average fatigue life of 6400 cycles at the very low glass content of 43.7 vol-%. This compares with a fatigue life of 5400 cycles for the standard composition at the usefully high glass content of 57.4 vol-%. Because of the great difficulty in maintaining good quality control of the amine-cured Epon 826 systems, no effort was made to conduct more experiments with these compositions. Neither did the hexahydrophthalic anhydride (HHPA) or 4,4'-methylene-bis-(2-chloroaniline) (MOCA) curing agents produce composites having properties attractive enough to warrant more extensive study.

Inherently Water-Resistant Epoxies

It was concluded from the foregoing experiments that when the glass constituted 60% or more by volume of the composite, and when the resin was a typical state-of-the-art bisphenol-A type, there was very little prospect of developing a unidirectional glass-fiber composite having a satisfactory fatigue life in water of 10,000 cycles at 280,000 psi maximum fiber stress. This conclusion indicated the need for more water-resistant resins. A "screening" search was made for such resins by conducting experiments on a variety of epoxies of substantially different composition. Resins selected for screening were known to be types that provided high-strength plastics, but their sensitivities to water were not known. The results of these experiments are shown in Table 9.

Four epoxy matrices of improved water resistance and better fatigue life than previously obtained were discovered (resin systems 6, 9, 10, and 11, Table 9). Only Shell's ERX-67 has received sufficient attention at this writing to warrant conclusions on its potential as a matrix for high-performance glass-reinforced plastics for marine use.

Table 8
The Effect of Curing Agent on the Physical Properties and Cyclic Fatigue Life in Water of NOL Rings Made With Epon 826 Resin

Curing Agent (phr)*	Curing Schedule (hr/°F)	Glass† (vol-%)	Voids† (vol-%)	Interlaminar Shear Strength† (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Range in Cycles to Failure	Average Life (cycles)
HHPA(80)/BDMA(1)	2/176;4/302	55.7‡	2.9	12,000	280,000	5	2200-4800	3100
MOCA(33)	3/248;16/320	62.0‡	1.2	12,600	280,000	6	4000-6000	5100
MPDA(12.5)	16/128;1/180	43.7‡	7.6	13,000	280,000	6	3700-9100	6400
MPDA(12.5)	3/338	57.7§	7.4	8,500	320,000	5	—	<1000
MABA(13)	16/77;1-1/2/150 2-1/2/300	61.4§	7.2	8,400	320,000	5	—	<1000
NMA(85)/BDMA(1)	2/225;2/275 2/330	58.3§	2.4	13,200	320,000	6	2400-4000	3100
NMA(85)/BDMA(1)	2/225;2/275 2/330	57.4‡	0.8	13,400	280,000	28	4600-6200	5400

*Parts per hundred parts of resin by weight.
†Value from ring of same lot.
‡Ferro S-1014 glass.
§Owens-Corning S-994 glass

Table 9
The Effect of Composition on the Physical Properties and Cyclic Fatigue Life in Water of NOL Rings

Resin System No.	Resin System Composition	Curing Schedule (hr/°F)	Glass*† (vol-%)	Voids* (vol-%)	Interlaminar Shear Strength* (psi)	Max Fiber Stress (tension) (psi)	No. of Rings	Range in Cycles to Failure	Average Life (cycles)
1	5868R prepreg	1/200;2/350	67.8	0.9	11,400	240,000	5	4000-5800	4,800
2	4617 prepreg	14/185;6/320;4/400	69.3	0.6	13,000	240,000	5	1600-3100	2,300
3	ERLB‡4617/MDA	—	65.1§	—	—	280,000	2	1700-3700	2,700
4	ERLB‡4617/MPDA	—	64.2§	—	—	280,000	2	2500-3500	3,000
5	Resorcinol-Epoxy/MPDA(22.5)¶	16/77;2/212; 2/257;2/302	54.4	5.3	9,200	260,000	3	2900-4600	3,600
6	ERL 2256/ZZL-0820 (27)¶	2/185;4/302	56.9	1.5	15,100	280,000	13	4300-7600	6,400
7	ERL-0400/MPDA(28)¶	2/212;6/320	59.0	<0.1	18,200	280,000	7	2200-2600	2,500
8	Epon 826/NMA(85)¶/BDMA(1)¶	2/225;2/275;2/330	57.4	0.8	13,400	280,000	28	4600-6200	5,400
9	ERL 2256/ZZL-0820(27)¶/Aroclor 1254(10)¶	2/185;4/302	55.5	1.6	16,000	280,000	7	9800-12,200	10,900
10	Velsicol DGEHQ/NMA(50)¶/BDMA(1.6)¶	2/248;20/356	50.8	2.3	12,200	280,000	7	4800-13,200	8,300
11	ERX-67/MPDA(10)¶	2/212;4/302	62.0	2.7	11,900	280,000	15	11,500-19,000	14,400

*Value from ring of same lot.
†Ferro glass unless noted otherwise.
‡Special washed ERLA 4617.
§Actual glass content; source of glass unknown; rings supplied by Union Carbide Corp.
¶Parts per hundred parts of resin by weight.

ERX-67 is N,N-bis(2,3-epoxypropyl) tribromoaniline. Shell reports the water pickup of ERX-67, cured with meta-phenylenediamine, to be approximately one-fifth that of their bisphenol-A epoxy, Epon 828, cured with the same agent. (Epon 828 is quite similar to Epon 826, the reference epoxy used in this study.) NRL has found the water adsorption of ERX-67 to be about one-third that of Epon 826 cured with nadic methyl anhydride. Figure 6 gives more specific data comparing the water absorption of ERX-67 with typical epoxies. The first determination of the fatigue qualities of glass-fiber composites made with ERX-67 using 62% glass by volume (38% resin) gave 14,400 cycles (Table 9). This is roughly 2-1/2 to 3 times the fatigue life obtained with the reference composition (resin system 8, Table 9). A number of additional experiments were conducted to determine the fatigue life of ERX-67 NOL rings having a range of resin contents. Tables 10 and 11 give

UNCLASSIFIED

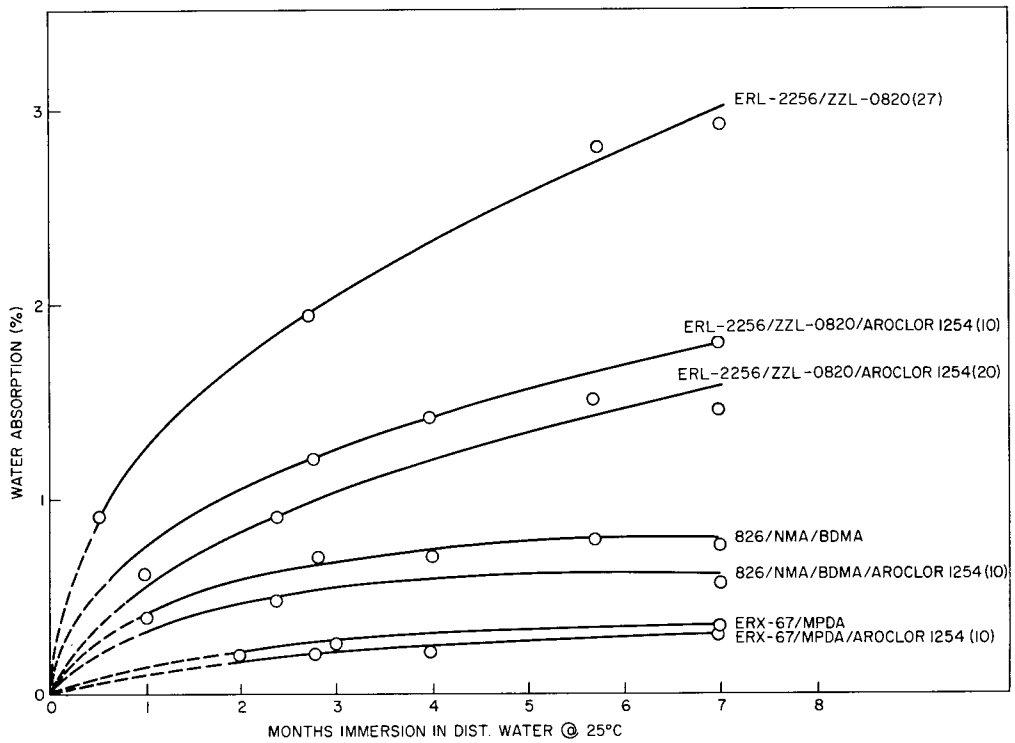


Fig. 6 - Water absorption of epoxy resins. The number in parentheses represents parts per hundred by weight of resin.

Table 10
Data on ERX-67/Glass-Fiber NOL Rings

Experiment No.	No. of Rings	Resin Content* (vol-%)	Fatigue Cycles in Water			Standard Deviation (cycles)	Coefficient of Variation (%)
			High	Low	Average		
ML166	7	31.7	6,200	4,100	5,000	860	17.2
ML169	7	34.6	6,600	4,700	6,000	700	11.7
ML161	6	34.8	7,800	6,000	7,000	710	10.3
ML158	6	37.4	9,000	6,000	7,800	1,000	13.2
ML167	7	37.8	8,000	4,700	6,400	1,100	17.6
ML122	6	38.6	13,800	11,500	12,900	810	6.3
ML115	5	40.0	18,500	15,000	16,800	1,530	9.1
ML123	5	42.6	15,000	12,600	13,800	1,130	8.3
ML174	7	44.2	14,800	9,200	12,300	2,400	19.6
ML173	7	45.6	17,100	13,200	15,700	1,560	9.6

*Glass content = 100 minus resin content, vol-% (voids neglected).

Table 11
Data on Epon 826/NMA/BDMA/Glass-Fiber NOL Rings

Experiment No.	No. of Rings	Resin Content* (vol-%)	Fatigue Cycles in Water			Standard Deviation (cycles)	Coefficient of Variation (%)
			High	Low	Average		
ML26	5	34.1	3,100	2,400	2,700	288	10.8
ML83	5	40.6	6,200	5,000	5,500	591	10.7
R8	28	41.8	6,200	4,600	5,400	901	17.0
ML79	6	42.9	7,300	5,300	6,300	896	14.2
ML94	5	44.5	5,800	5,200	5,500	279	5.0
ML93	7	44.8	5,000	3,000	4,300	717	16.7
ML8	5	54.1	12,500	6,600	9,700	2,478	25.4

*Glass content = 100 minus resin content, vol-% (voids neglected).

the data on this series of experiments as well as data on a like series of experiments with the reference composition. Figure 7 graphically illustrates the data. The advantage of the more water-resistant resin is obvious. Void content in all of these rings ranged between 1 and 3% and usually was 2% or slightly less.

One disadvantage of ERX-67 is its high density, about 1.8 as compared to densities ranging between 1.2 and 1.3 for typical state-of-the-art, bisphenol-A epoxy resins. This fact will have to be taken into consideration in some uses of ERX-67. Figure 8 presents an interpretation of the data computed from Fig. 7 correlating fatigue life with the density of GRP over a range of glass-to-resin ratios.

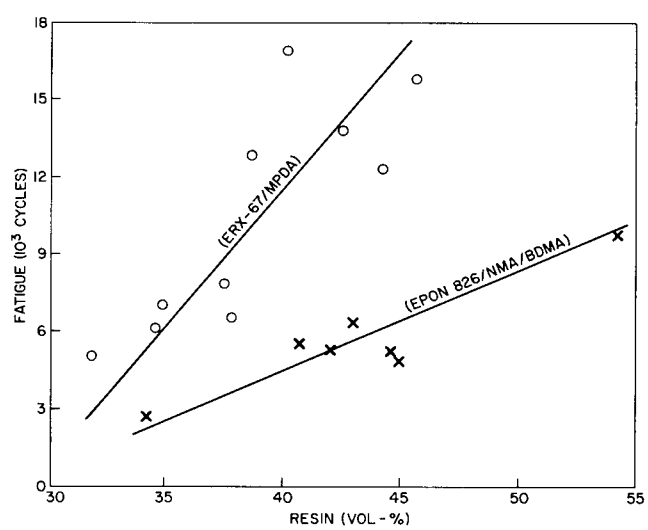


Fig. 7 - Effect of resin on fatigue of GRP in water. The maximum fiber stress was 280,000 psi.

UNCLASSIFIED

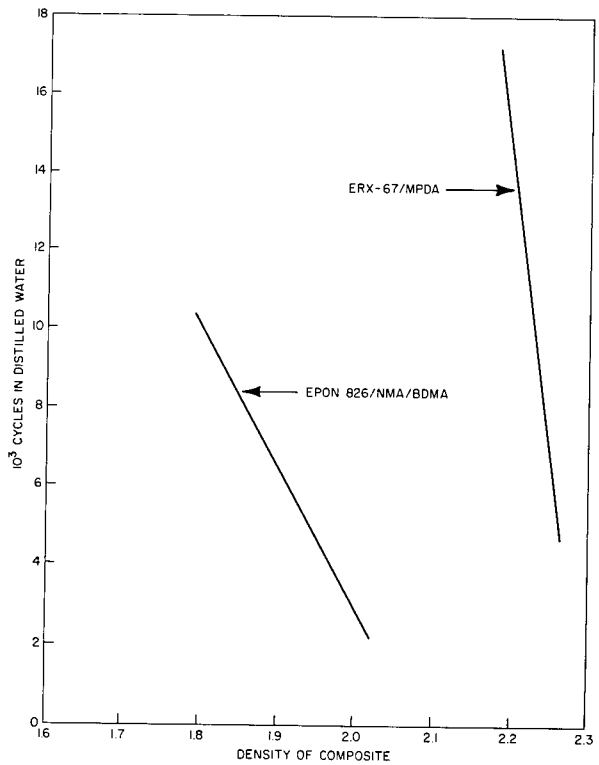


Fig. 8 - Correlation of fatigue life with the density of GRP using Epon 826 (sp gr 1.2) and ERX-67 (sp gr 1.8)

DISCUSSION

The experiments described in this report provide convincing evidence of the severity of water, as compared to air, in limiting the dynamic fatigue life of glass-fiber-reinforced epoxy plastics. Other work at NRL and elsewhere has firmly established the vulnerability of both the glass-fiber and the glass-fiber-to-resin bond to degradation by water (9,10,32, 33). In short, water readily attacks the total composite material—the matrix, the matrix/fiber interface, and the fiber itself when the latter is glass. Just which element of the composite is most vulnerable to aqueous attack is debatable. Probably the answer is different for each different combination of the components.

This work also shows that epoxy resins suffer accelerated degradation by water when they are subjected to high stresses. Further, dynamic stresses in combination with water are 10 to 100 times as damaging as static stress. The fact that the susceptibility of different epoxies to hydrolytic attack varies widely suggests a close relationship between this susceptibility and molecular composition. And, the relative severity of water, as compared to air, in limiting the fatigue life of GRP suggests the possibility that water may induce a stress-corrosion-like failure in the composite material.

Obviously the function of the resin in a composite includes distribution of stresses between fibers as well as protection of the reinforcement from a hostile environment. Hence, the integrity of the resin is essential to sustained performance of the composite material. The resistance of the resin to fracture (cracking) under stress is, in part, a function of the intrinsic ability of the resin to withstand at least as much strain as is imposed on the reinforcement. Flaws that occur in fabrication and adverse effects of the

environment increase the burden on the matrix. Therefore, the effectiveness of the resin in the composite material is the result of at least its mechanical properties and environmental stability acting in unison.

NRL's search has resulted in the discovery of at least one epoxy composition (Shell's experimental ERX-67) of decidedly better water resistance than the epoxies now typically used in GRP. Additionally, a plasticized epoxy matrix (i.e., ERL 2256/ZZL-0820/Aroclor 1254) has afforded a composite having significantly better fatigue resistance than the reference composition in water, though not equivalent to GRP using the more water resistant ERX-67.

At first glance, these findings would seem to indicate that a more systematic and searching application of chemistry might yield resins that could even better enhance the reliability of structural composites in marine use. A deeper analysis does not refute this possibility but does predict that major new progress on a technological scale may be rather distant because of both scientific and cost considerations. The phenomenally low water absorption of ERX-67 is likely to be improved upon only by highly fluorinated compositions. While some fluorinated epoxies are known, the technology for their large-scale commercial production is not developed, and they are very costly.

This work, in combination with that of other researchers, appears to have established a foundation from which a more fundamental and analytical course could be followed to advance the state-of-the-art of fiber-reinforced composites. Tsai (34) and Halpin (35) have shown that there is enough fundamental knowledge of temperature effects on the viscoelastic properties of solid polymers to reasonably predict their time-dependent mechanical behavior over a considerable temperature range. Tsai and Halpin postulate —by analogy—that the swelling effect of water on solid polymers might similarly be correlated with mechanical behavior. Anderson (36) derived a quantitative relationship between matrix properties, including temperature effects, and the torsional fatigue life of filament-wound segments of NOL rings in the "dry" condition. Anderson also showed that the effect of water on the fatigue life of his specimens was extremely severe, but he made no attempt to extend his fundamental derivations to include the aqueous environment. And, Quackenbos and Hill achieved some success in relating water absorption to mechanical damage in phenolic plastics (37).

CONCLUSIONS

Two important effects of water absorption by plastics are generally recognized: (a) that mechanical properties change and (b) that all dimensions expand. We have seen the macrodegradation of GRP resulting from cracks in the matrix, accelerated by water; but aside from diffusion, the molecular processes accompanying this failure are not understood. It is generally conceded that water may attack a polymer in at least two ways: (a) by plasticization, which is a reversible process, but more importantly (b) by total, or very severe "corruption" of the polymer's molecular structure, which is an irreversible process. The latter may include both chemical reaction and absorption and "stress-corrosive" acceleration of flaw growth.

There is yet insufficient knowledge of these processes, particularly the second, to reasonably predict the engineering response of composite materials to water. However, the information now existing from many sources strongly suggests that there is a determinative but yet undiscovered relationship between the time-dependent response of a composite material to stress and the degradation of its matrix by hydrolytic and other processes. Knowledge of such a relationship would greatly increase confidence in the use of these materials, and their true potential then could be fully exploited. It is concluded that the evidence now accumulated affords a promising basis for a unified research effort in chemistry and mechanics to gain this knowledge.

UNCLASSIFIED

ACKNOWLEDGMENTS

The authors are indebted to Dr. J.R. Griffith for his most helpful advice and guidance throughout this work. The authors also thank Mr. Francis Faith of the Ocean Technology Division and Mr. Clinton Sansbury and Mr. Frank Lagana of the Engineering Services Division for winding most of the NOL rings. Thanks are also given to the Engineering Services Division for finish-grinding and segmenting the rings and to Mr. Charles Herbert of the Electronics Division for preparing the specimens for void count studies.

The authors are grateful to the Naval Ordnance Laboratory for winding the NOL rings made with prepreg.

REFERENCES

1. Whisenhunt, F.S., Jr., "Filament-Winding Plastics, Part 2—Role of the Resin in Glass-Fiber-Reinforced Structures Under Tensile Stress," NRL Report 6161, Dec. 1, 1964

2. Griffith, J.R., "Filament-Winding Plastics, Part 3—Some Effects of Curing Agent Structure Upon Epoxide Plastic Physical Properties," NRL Report 6313, Sept. 13, 1965

3. Griffith, J.R., "Filament-Winding Plastics, Part 4—Syntheses, Properties, and Uses of m-Aminobenzyl Amine (MABA)," NRL Report 6439, Oct. 25, 1966

4. Sands, A.G., Clark, R.C., and Kohn, E.J., "Microparticle and Fiber Reinforcement of Epoxy Resin," NRL Report 6403, Aug. 26, 1966

5. Griffith, J.R., and McGraw, M.E., "Filament-Winding Plastics, Part 5—Epoxy Amine Reactions and the Practical Use of High-Strength Plastics," NRL Report 6690, Apr. 10, 1968

6. Bascom, W.D., "Some Surface Chemical Aspects of Glass-Resin Composites, Part 2—The Origin and Removal of Microvoids in Filament-Wound Composites," NRL Report 6268, May 24, 1965

7. Bascom, W.D., and Romans, J.B., "Microvoids in Glass-Resin Composites," Ind. Eng. Chem. Prod. Res. Dev. 7:172 (1968)

8. Kohn, E.J., Sands, A.G., and Clark, R.C., "Quantitative Measurement of Void Content in Glass-Filament-Wound Composites and Correlation of Interlaminar Shear Strength with Void Content," Ind. Eng. Chem. Prod. Res. Dev. 7:179 (1968)

9. Zisman, W.A., "Surface Chemistry of Plastics Reinforced by Strong Fibers," Ind. Eng. Chem. Prod. Res. Dev. 8:98 (1969)

10. Bascom, W.D., "Water at the Interface," J. Adhesion 2:161 (1970)

11. Kies, J.A., "Maximum Strains in the Resin of Fiberglass Composites," NRL Report 5752, Mar. 26, 1962

12. Broutman, L.J., and Krock, R.H., Editors, "Modern Composite Materials," Reading, Mass.:Addison-Wesley, 1967

    a. Chapter 2, p. 96, Corten, H.T., "Micromechanics and Fracture Behavior of Composites"
    b. Chapter 11, p. 307, Lowrie, R.E., "Glass Fibers for High-Strength Composites"
    c. Chapter 1, p. 17, Krock, R.H., and Broutman, L.J., "Principles of Composites and Composite Reinforcement"

13. Fried, N., "Degradation of Composite Materials: The Effect of Water on Glass-Reinforced Plastics," Mechanics of Composite Materials, Proceedings of the Fifth Symposium on Naval Structural Mechanics, edited by F.W. Wendt, H. Liebowitz, and N. Perrone, New York:Pergamon, pp. 813-837, 1970

14. Data supplied by manufacturer.

15. Lee, H., and Neville, K., Chapter 12 in "Handbook of Epoxy Resins," New York: McGraw-Hill, 1967

16. Fried, N., Kaminetsky, J., and Silvergleit, M., "The Effect of Deep Submergence Operational Conditions on Filament-Wound Plastics," 21st Technical Conference, The Society of the Plastics Industry, 1966

17. Abbott, B.W., Cornish, R.H., and Cole, C.K., "Effect of Cycle Profile on the Biaxial Compressive Fatigue Performance of Filament-Wound Laminates," Technical Summary Report M6081, IIT Research Institute, Technology Center, Chicago, Ill., Jan. 1965

18. "Symposium on Standards for Filament-Wound Reinforced Plastics," ASTM Special Publication 327, American Society for Testing and Materials, Philadelphia, Pa., 1963

    a. Prosen S.P., Karpe, S., Kinna, M.A., Mueller, C., Perry, H.A., and Barnet, F.R., "Compression, Fatigue, and Stress Studies on NOL Ring Specimens," p. 105
    b. Roskos, T.G., and Pflederer, F.R., "The NOL Ring Test as a Method for Selecting Finished Glass Fibers for Reinforcement of Epoxy Pipe," p. 96

19. Union Carbide Corporation, Final Report "Research on Improved Epoxy Resins," Contract NOnr-4172(00)(X), Nov. 1, 1968

20. ASTM Designation D 2291-67, "Fabrication of Ring Test Specimens for Reinforced Plastics," Annual American Society for Testing and Materials Standard, Part 26, July 1970

21. Battelle Memorial Institute, "Mechanism of Water Absorption in Glass-Reinforced Plastics, Contract NObs 86871, Project SR-007-03-04, Task 1008, BuShips 98-1008-10 (1962-63)

22. Glowacki, A.S., and MacDonald, D.C., (United States Rubber Company, Research Center) "Protective Coatings for Filament-Wound Deep Submergence Vessels," Final Report Contract NObs-90246 for Bureau of Ships, Mar. 1965

23. Herrick, J.W., "The Permeability of Plastic Films Exposed to Pressurized Fresh and Salt Water," AVCO Corporation Technical Memorandum RAD-TM-64-8, Feb. 1964

24. Acharya, Y.V.G., Srinath, L.S., and Lakshminarayana, C.N., "Evaluation of Stresses in a Circular Ring by the Relaxation Method," Appl. Sci. Res., Vol. A3:415-428 (1953)

25. Chayes, F., "Petrographic Modal Analysis," New York:Wiley, 1956

26. ASTM Designation D 2344-67, "Apparent Horizontal Shear Strength of Reinforced Plastics by Short Beam Method," Annual American Society for Testing and Materials Standards, Part 26, July 1970

27. McGarry, F.J., "Crack Propagation in Fiber Reinforced Plastic Composites," Swartz and Swartz, editors, New York:Interscience, p. 63, 1968

UNCLASSIFIED

28. Epstein, G., and Banderuk, W., "The Crazing Phenomenon and its Effects in Filament-Wound Vessels," 19th Annual Meeting, Society of the Plastics Industry, Feb. 1964

29. Laird, J.A., and Nelson, F.W., SPE Trans., p. 124, Apr. 1964

30. Moilliet, J.L., editor, "Waterproofing and Water-Repellency," New York:Elsevier, p. 209, 1963

31. Bulletin 0-P-115, "The Aroclors," Monsanto Chemical Company, St. Louis, Mo.

32. Schmitz, G.K., and Metcalfe, A.G., "Stress Corrosion of E-Glass Fibers," Ind. Eng. Chem. Prod. Res. Develop. 5(No. 1):1-8 Mar. 1966

33. Schmitz, G.K., Gulden, M.E., and Metcalfe, A.G., "A Study of Stress Corrosion of Glass Fibers; Part II—Effect of Glass Composition," Contract N00019-69-C-0145 for Naval Air Systems Command, Final Report, Feb. 1970

34. Tsai, S.W., "Environmental Factors in the Design of Composite Materials," Mechanics of Composite Materials, F.W. Wendt, H. Liebowitz, and N. Perrone, editors, New York: Pergamon Press, pp. 749-767, 1970

35. Halpin, J.C., "Introduction to Viscoelasticity," Composite Materials Workshop, S.W. Tsai, J.C. Halpin, and N.J. Pagano, editors, Stanford, Conn.:Technomic pp. 87-152, 1968

36. Anderson, R.M., "Some Major Factors Controlling Torsional Fatigue Life of Fiber Reinforced Plastic Composites," Contribution HPC66-16, Monsanto/Washington University ARPA Project—High Performance Composites, 1966

37. Quackenbos, H.M., Jr., and Hill, J.M., "Effect of Absorbed Water on Physical Properties of Phenolic Plastics," Trans. ASME 74:41-50, Jan. 1952

UNCLASSIFIED

Security Classification

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
FATIGUE BEHAVIOR OF GLASS-FILAMENT-WOUND EPOXY COMPOSITES IN WATER

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
An interim report on a continuing NRL problem.

5. AUTHOR(S) *(First name, middle initial, last name)*
J.B. Romans, A.G. Sands, and J.E. Cowling

6. REPORT DATE
April 5, 1971

7a. TOTAL NO. OF PAGES
26

7b. NO. OF REFS
37

8a. CONTRACT OR GRANT NO.
NRL Problem C03-19

b. PROJECT NO.
SF 51-544-102-12432

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Report 7246

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT
[redacted]

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY
Department of the Navy (Naval Ship Systems Command), Washington, D.C. 20360

13. ABSTRACT

The significance of matrix compositions has been studied in relation to the fatigue characteristics of glass-filament-wound reinforced plastics. Evidence indicates that water, as compared with air, severely limits the dynamic fatigue life of glass-reinforced epoxy plastics. It is suggested that a relationship may exist between matrix degradation and the time-dependent response of the composite material to dynamic stresses. A new, very-water-resistant epoxy resin is shown to increase the reliability of glass-fiber-reinforced plastic by 200 to 300% in comparison with an equivalent state-of-the-art composition exposed to the same type of stress and environmental conditions.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Glass-fiber-reinforced plastics						
Fatigue						
Hydrolytic attack						
Water-resistant epoxy resin						