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Performance of Plastics in Water Environments

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The technology of reinforced plastics has advanced to where these materials are candidates for structural use in water environments. The commercial boat industry and several Navy applications have shown us where the problem areas are and taught us the importance of good quality control during fabrication. Water-absorption problems confront us when we consider this material for underwater use. The water most likely diffuses into the material at the interface of the reinforcement and the matrix. In order to overcome this, we have done research work to improve the bond between the reinforcement and the matrix. We have learned to make better bonds and better all-around composites. These well-made composites, when subjected to creep and fatigue loads in water, stand up very well.

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INTRODUCTION

The technology of reinforced plastics is growing and is providing the designer, the architect, and the user with a new class of materials having extraordinary properties. Glass reinforced plastics, for instance, provide strength-to-weight and modulus-to-weight ratios greater than most materials. They are inherently resistant to corrosion; they are nonmagnetic and possess good dielectric properties besides being readily fabricated into large structures of complex shapes. Although reinforced plastics structures have been extremely successful for many applications, these materials have not reached their full potential under compressive or external loadings in water, such as those experienced in deep submergence. This fact does not indicate an inherent limitation of reinforced plastics but reflects the present state-of-the-art of reinforced plastics structures.

On the other hand, many discuss the promise of these materials (1, 2, 3).[1] With the advent of the new reinforcing fibers, such as boron, the carbides and/or the graphites, and with the advances in resin technology, we foresee even greater use of reinforced plastics in marine environments. The high strength-to-weight and modulus-to-weight ratios of the new fibers when combined with plastics make them very attractive. Many have shown the advantages of these new fibers in many structural applications, including deep submergence structures, where lightweight, high modulus, and high strength are important (4, 5, 6, 7).

The Navy is also contemplating more use of these structural materials to the very depths of the ocean. Because of this, it is imperative that we know more about the effects of water on these materials. This report will attempt to bring us up-to-date on the structural use of these materials in water and how these reinforced plastics materials are affected by the water environment, especially when subjected to the stresses of deep submergence. Many researchers have reported on water absorption, creep and fatigue, both cyclic and static, as well as design considerations of these materials; this report, however, will point out the significant findings of the various studies and discuss some studies done at the Naval Ordnance Laboratory in this field.

REINFORCED PLASTICS "IN WATER"

The advantages in using these materials for marine service have resulted in various applications of reinforced plastics -- the plastic boat industry is one that can be cited for being very successful. Another application cited by N. Fried and W. Graner (8) is the success of a reinforced-plastic fairwater for the submarine USS "Halfbeak." The elements of this fairwater were assembled and installed aboard the "Halfbeak" in 1953 and entered into service early in 1954. After some 11 years of service, the plastic fairwater was removed from the vessel. Samples were cut from the various sections of the fairwater and submitted to tests. The data, both the original, after molding, and after 11 years of service are shown in Table 1. The success of reinforced plastics in this environment is indicated by the lack of degradation of properties as seen in the table. This direct evidence of the permanence of glass-reinforced plastics in a marine environment provided by this "Halfbeak" investigation, as well as some of the other structures (floats, boats, and so forth) made of this material, gives us an indication of the durability of this material in the water environment and indicates that we can rely on it for use for long periods of time and under wet conditions.

REINFORCED PLASTICS "UNDERWATER"

One of the Navy's first external pressure vessels made of these materials is the Mark 57 Mine Case (Fig.1). This mine case was made of glass fabric and epoxy resin. The design problems, such as end closures, openings and joints, as well as performance problems, such as resistance to shock loads, long-term loads and moisture transmission, were worked out on this mine case. The result of this study was a mine case incorporating performance characteristics unique with a glass-reinforced plastics construction, yet capable of serving as a primary structure under long-term external loading conditions in a sea

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[1] Numbers in parentheses designate References at the end of the paper.

TABLE 1

EVALUATION OF REINFORCED PLASTICS FAIRWATER

ON USS HALFBEAK--SUMMARY OF DATA

Property	Condition	Original Data[2]	Current Data (eleven years service) Panel 1	Panel 2	Avg.	Specification Requirement[b]
Flexural strength, psi	Dry	52,400	51,900	51,900	51,900	50,000
	Wet[c]	54,300	46,400	47,300	46,900	45,000
Flexural modulus, psi x 10^6	Dry	2.54	2.62	2.41	2.52	2.50
	Wet	2.49	2.45	2.28	2.37	2.30
Compressive str., psi	Dry	-	40,200	38,000	39,100	33,000
	Wet	-	35,900	35,200	35,600	28,000
Barcol hardness	Dry	55	53	50	52	-
Specific gravity	Dry	1.68	1.69	1.66	1.68	-
Resin content, %	Dry	47.6	47.4	48.2	47.8	35-43

a Average of three panels
b MIL-P-17549
c Two-hour boil

NOTE: This table was taken from reference 8.

Fig. 1 Reinforced-plastic underwater mine case

water environment. The development of that case is discussed in a Navy report (2).

History has shown that the success of the mine case was dependent upon the care and the quality control procedures used in making the case. The porosity and void population of the laminate in the case is controlled by fabrication procedures; good fabrication techniques and close control produced a mine case that resisted external pressure with no leaks and no failures. In fact, the shock resistance of a well-fabricated case was much better than one in which voids and porosity existed. Mine cases which had porosity problems, starved or resin rich areas, or fibers which were not thoroughly wetted by the resin eventually would leak under external hydrostatic pressure.

WATER ABSORPTION

Several studies have shown that water does affect the properties of reinforced plastics materials. The mechanism of how it degrades the material is not understood and many theories exist. Glowacki (9) stated that cast epoxy showed a strength loss up to 15 percent after exposure to hot water, but the strength recovered after drying; thus moisture has a plasticizing effect. This same effect of water was shown by Krolikowski (10). In other studies of the mechanisms of water absorption (11) it is stated that moisture absorption in cast epoxy resin cylinders for 1600 hr showed weight increases of 5 mg/g with no variation in absorption due to pressure at 10,000 psi. Filament wound cylinders, on the other hand, gave more erratic moisture pickup results, the total accumulation being 3 to 5 mg/g in 1600 hr. The aforementioned studies give us the clue that in building composites we have to be very careful, we must have less voids and we must get good wetting. In this way, water will be less likely to diffuse along the fibers at the interface. Lebovits (12) stated that hydrostatic pressure has only a small effect on plastics except for flow through cracks or pores and that the diffusion rate along the glass fiber epoxy interface was 450 times faster than through the resin.

The previous discussions serve to illustrate the importance of high quality laminates (low void content) on the permanence properties of these structural materials. The mine case is a product of the mid 1950's and the technology then was, of course, not so far advanced as it is today. The curves of Fig.2 show the water permeability improvement as seen by tests on two cylinders (Fig.3), one made in 1955 and one made just over two years ago. The moisture transmission rate is quite different for the two cylinders. The number of grams transmitted through the walls of this nominal 10-in. cylinder, with a 1/4-in. wall, is only 9 g in 140 weeks, whereas the water transmission curve of the cylinder fabricated in 1955 using the materials and the technology of that day would have reached 9 g in about 35 days. This portrays an increase in the water resistance brought about by better technology, which in turn has brought about lower voids, better wetting, and a better laminate.

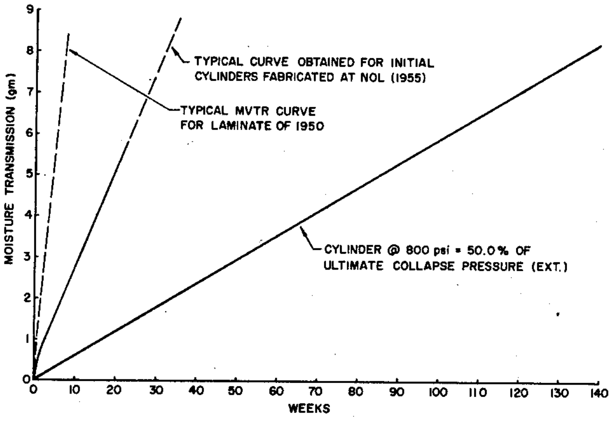

Fig. 2 Water permeability of glass-reinforced plastic structures under external hydrostatic pressure

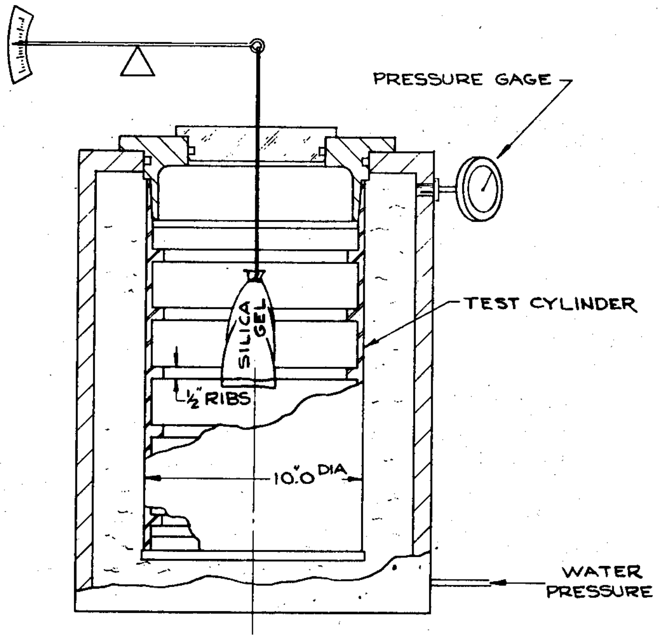

Fig. 3 Long-term hydrostatic pressure test on cylinders

RING, UNIAXIAL WET FATIGUE

With the success of the mine case and with

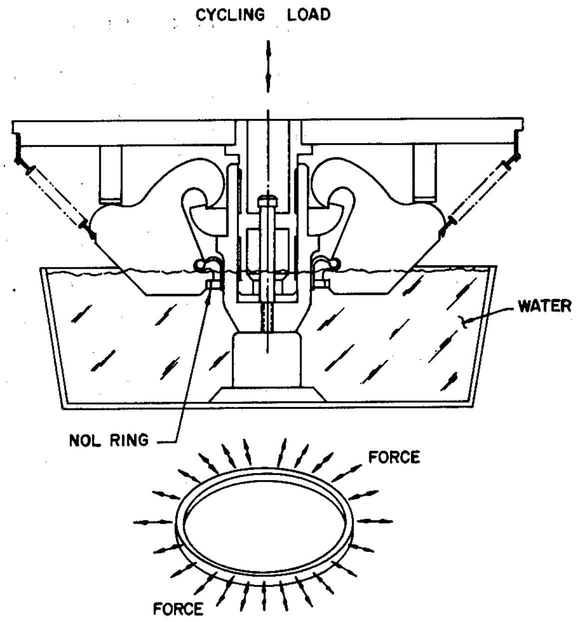

Fig. 4 Wet compressive fatigue test for NOL rings

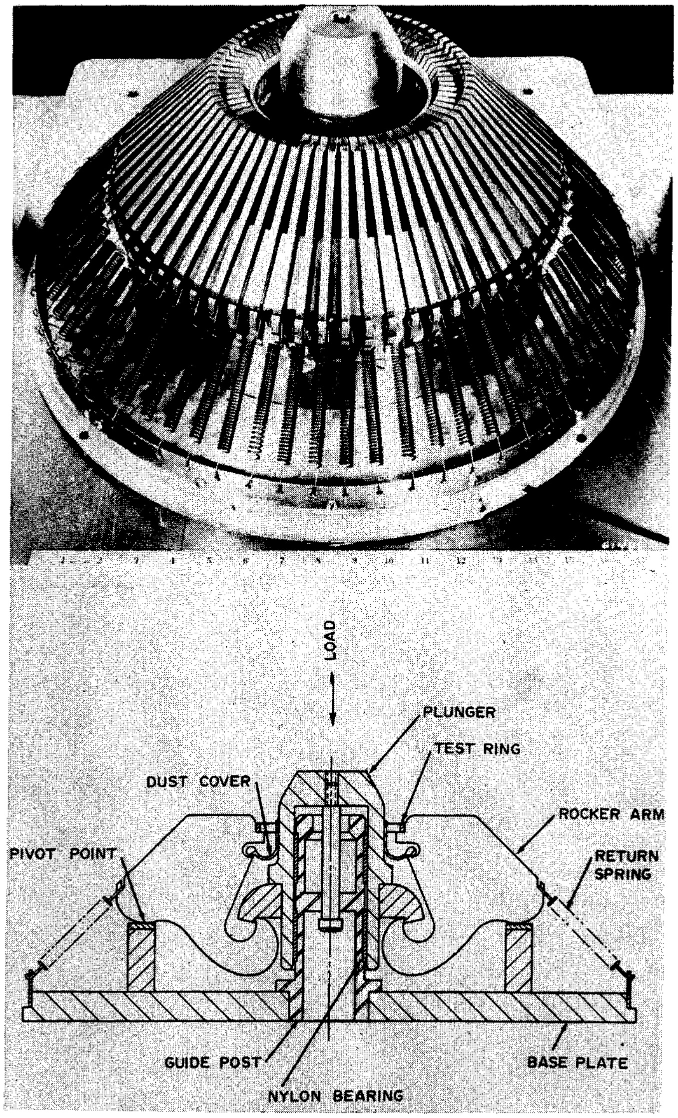

Fig. 5 Schematic diagram of ring compression tester

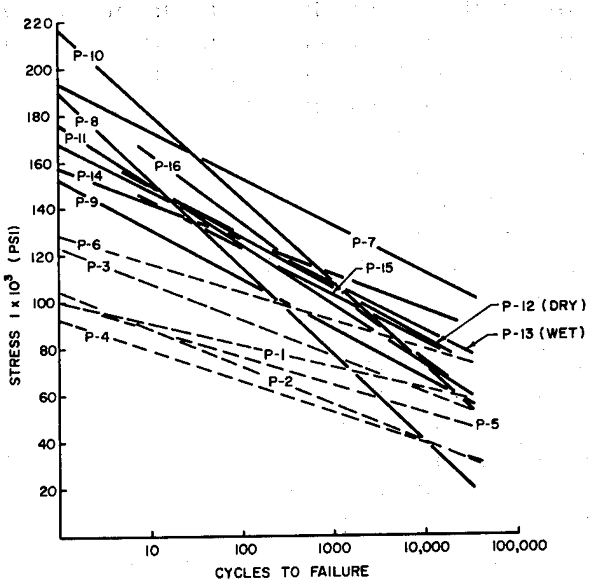

Fig. 6 Immersed cyclic compression of NOL rings

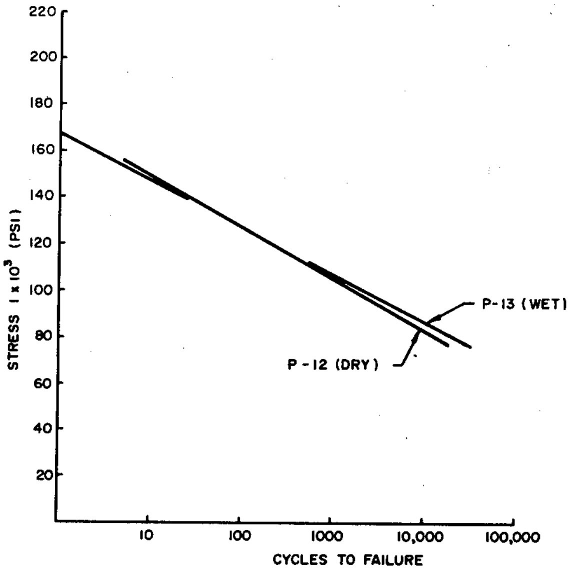

Fig. 7 Wet and dry cyclic compression of NOL rings

a better understanding of the properties of reinforced plastics materials under compressive and shear loads, programs of assessing their potential for deep-diving submersibles were originated. The programs were designed to assess these materials in terms of water absorption, creep under sustained wet load, fatigue, both wet and dry, and other life studies.

In a study carried on by the A. O. Smith Corporation, Milwaukee, Wis., for the Naval Ordnance Laboratory, NOL Rings were subjected to compressive fatigue in water (Fig.4). The fixture used to stress the rings is shown in Fig.5 and previously described by the author (13). Sixteen materials (Table 2) were tested over a period of several years; the fatigue curves are shown in Fig.6. The curves labelled P1 through P6 represent rings made by an early winding process which was lacking in precise control. This process led to resin richness and to a high number of uncontrolled voids. The curves of P7 through P16 represent the fatigue life of rings made with close control during winding. The improvement in fatigue life due to being further along the "learning curve" and due to closer control is obvious.

Fig.7 depicts two curves from Fig.6 and shows the fatigue curves of two series of like rings, one tested dry and one tested in water. The effect of testing in water is nil. This nil effect is due most likely to the uniaxial stress (along the fibers) applied by this tester which primarily stresses the fibers and not the interface. This stressing does not bring about the microcracks at the interface where water is likely to diffuse.

RING, MULTIAXIAL WET FATIGUE

In another study at NOL, we have developed a Multiaxial Fatigue Test (14) which subjects one half of the NOL Ring (a parallel filament wound ring) to a twisting moment (Fig.8). This twisting puts a stress on the interlaminar bond. The amount of resistance to this twist is a direct measure of this bond, and any degradation that

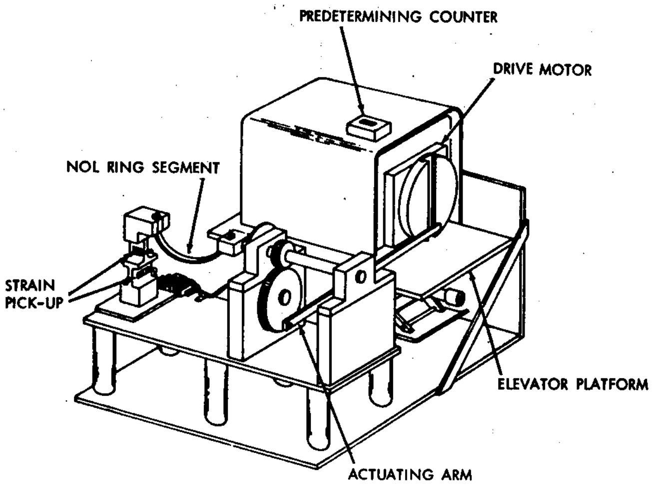

Fig. 8 NOL multiaxial fatigue tester -- schematic of functioning parts

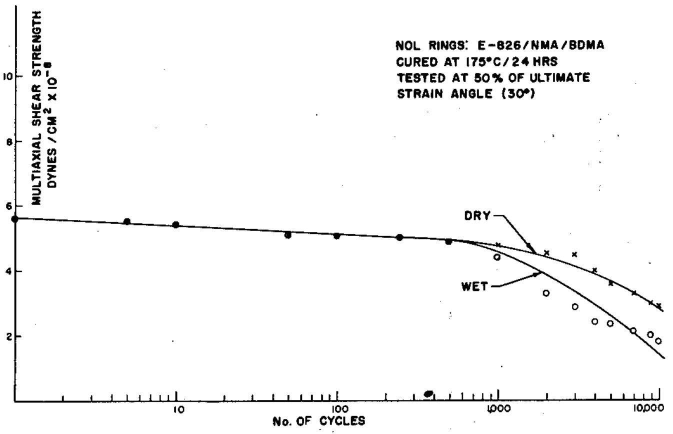

Fig. 9 Dry versus wet multiaxial fatigue testing of NOL rings

TABLE 2

MATERIALS IN UNIAXIAL COMPRESSION FATIGUE TEST

Group Nomen	Resin System
P-1	E-787 Prepreg (U. S. Polymeric)
P-2	A-46-S (RIPCO Prepreg)
P-3	E-826/MNA/BDMA (100/85/1) (wet system)
P-4	A-135-A (RIPCO Prepreg)
P-5	A-135-B (RIPCO Prepreg)
P-6	E-787 Prepreg (U. S. Polymeric)
P-7	ERX-36 (Shell Chemical Co.)
P-8	E-787 (Shell Chemical Co.)
P-9	Epycryl E11-S-75 (Shell Chemical)
P-10	ERL 0400 (Union Carbide)
P-11	E-717 (Shell Chemical Co.)
P-12	E-787 (dry) (Shell Chemical Co.)
P-13	E-787 20-end S994/HTS Prepreg
P-14	EF2 Prepreg (Cordo Chemical)
P-15	Y1-020-S-1014 Glass Roving ERL 2256/0820
P-16	Y1-020-S-1014 Fiberfoamed Glass Roving ERL 2256/0820

NOTE: All specimens were made with "S" glass roving, unless otherwise noted.

may occur at this bond (the interface of matrix and the reinforcement) shows up as a loss in measured stress.

In one set of experiments, the fatigue life at 20 cpm of rings tested at ambient conditions and of rings tested in water is plotted (Fig.9). As can be seen, even under this severe stress, the fatigue life at 50 percent of ultimate strength of rings tested wet is not too different below 1000 cycles from the dry or ambient test. After 1000 cycles, the two curves separate, showing that the degradation occurred at this time and that water aided and catalized this degradation.

The degradation in water using this multiaxial fatigue test is much greater than that to be experienced in the uniaxial compression fatigue test described earlier.

The effect of water on performance is much greater in the multiaxial fatigue test than in the uniaxial compression test. It is postulated that the multiaxial test attacks the weak portion of the composite (the interface) directly, thereby accentuating any weakness due to nonwetting or poor bonding on the fiber and the matrix that may have occurred. The uniaxial test accentuates and stresses the strength of the fiber and in this manner minimizes water effects.

CYLINDERS, HYDROSTATIC PRESSURE EFFECTS

In another study by Fried et al. (15, 16), the effects of the extended water immersion on reinforced plastics at various hydrostatic pressures up to 13,300 psig (which is equivalent to approximately 30,000 ft) were assessed. They showed that the effects of water immersion on the properties of this type of material are essentially independent of hydrostatic pressure; that is, immersion to 13,300 psig affects the material no more severely than exposure to 0 psig. They also showed that certain compositional factors, such as type of resin system, markedly influence the sensitivity to water. This study, as well as many others we will discuss later, shows that void content was a controlling factor in the effect of water resistance. For instance, laminates of good quality and reasonably low void content (less than 1.5 percent by volume) are relatively insensitive to water and that even after extended exposure under the most severe conditions the material in the "wet" condition retained over 90 percent of its initial dry mechanical strength (Fig.10). The authors point out that the key point in acquiring a composite material, which is quite resistant to water under even the most severe conditions, is quality and in this regard they say the void content is the principal factor.

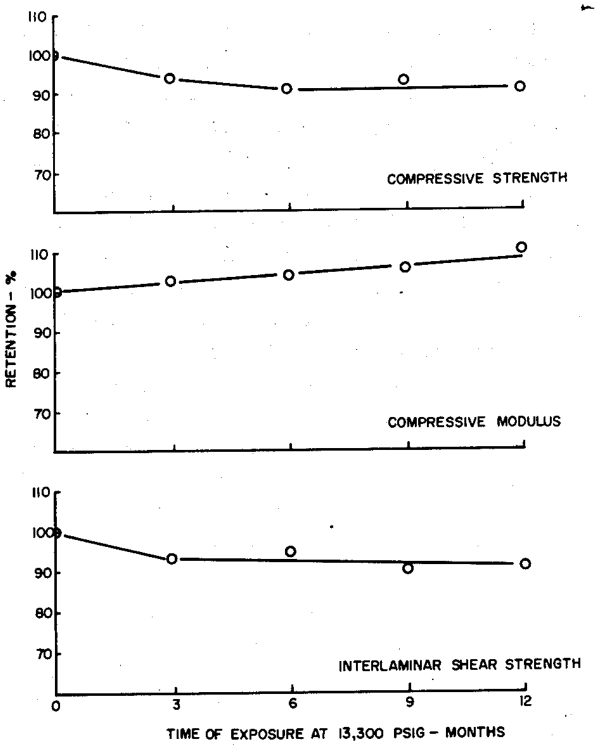

Fig. 10 Effect of time of exposure at 13, 300 psig on standard filament-wound plastic material (9)

The adverse affect of void content on the mechanical properties has also been demonstrated by Paul (17), Fried (18), and Prosen et al. (19). The authors say it is apparent that excessive void content has a deleterious effect on water resistance. This is borne out, especially in the fatigue studies that were carried on in Fried's work. The water absorption of filament wound materials of low void and high void is pictured in Fig.11, and the effect of void content on fatigue life is shown in Fig.12. The authors emphasized that the above trends are applied to present-day materials and it should be recognized that filament wound plastics, as well as other reinforced plastics, are relatively new. We, therefore, can expect with continued research highly improved composites, and these improvements will be typified by lower void content, better wetting, better shear strengths, which will further enhance the use of these materials in water and in deep-sea environments.

Others such as Freund and Silvergleit (20) stress the importance of interlaminar shear on the life expectancy of reinforced plastics materials. The authors related this shear strength to void content as well as other controlling processing factors and inferred a relationship between void content and fatigue life.

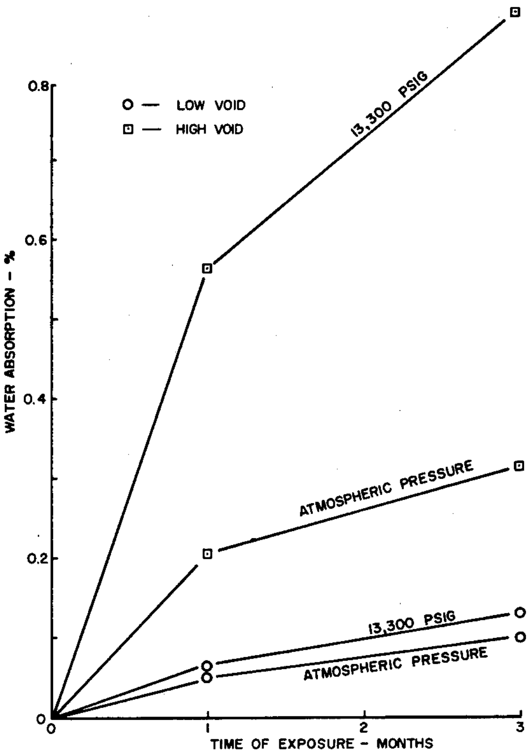

Fig. 11 Effect of time of exposure at various pressures on specially fabricated low and high-void filament-wound plastic material (9)

CYLINDERS WET FATIGUE

The Illinois Institute of Technology Research Institute (IIT) (21) has been carrying on fatigue studies on reinforced plastics (filament wound) cylinders. A typical fatigue curve of many specimens from various vendors is shown in Fig.12. The authors state that it is notable that a coefficient of variation of 3.86 percent was obtained for this compressive strength even with all the indicated variables present. They further state that the compressive strength of good quality reinforced plastics structures exhibits good consistency. The data of Fig.13 indicate by the relatively low spread that good consistency is obtained in the fatigue results.

The above fatigue work indicates that an average cycle life in wet environment of 10,000 can be expected between stress levels of 70,000 and 90,000 psi.

SUMMARY

Throughout the years we have learned how to fabricate reinforced plastics; we are still learning. The effect of "being further along the learning curve" has markedly affected the performance of these plastics materials in water environments. The better glasses, the better reinforcements, the better resins, and the better technology fabrication and design all give us hope that these materials with their high strength, high modulus, and low weight characteristics can be useful for structural purposes in water and in other environments.

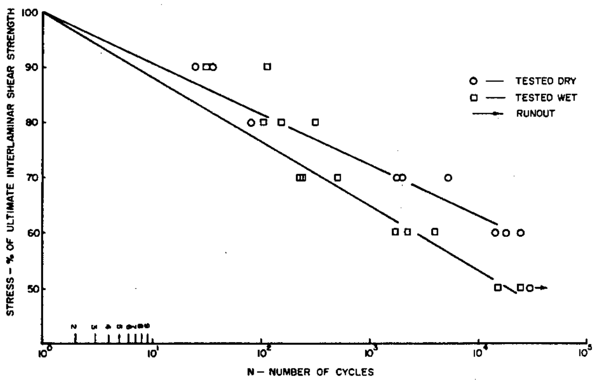

Fig. 12 Interlaminar shear fatigue curve for 2:1 orthogonal filament-wound plastic material (9)

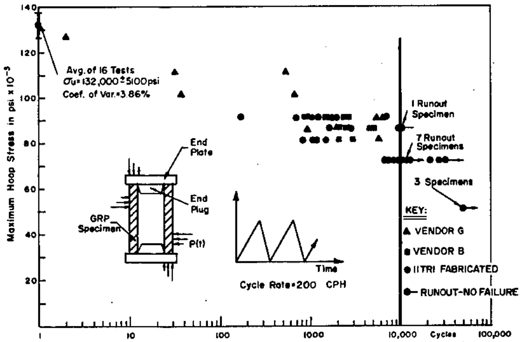

Fig. 13 Biaxial compressive fatigue data S994 glass, 20 percent - 828/1031 resin content, 2C:1L filament dispersion total of 79 specimens (20)

It seems then that to keep these materials useful and to get better and better performance we have to improve wetting, we have to improve interlaminar bond strength, we have to improve interlaminar shear, and, of course, we have to improve the reproducibility of samples. We have to know what our resin content is at all times, we must know what our void content is, and we in turn must know how to test for these nondestructively as well as destructively.

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