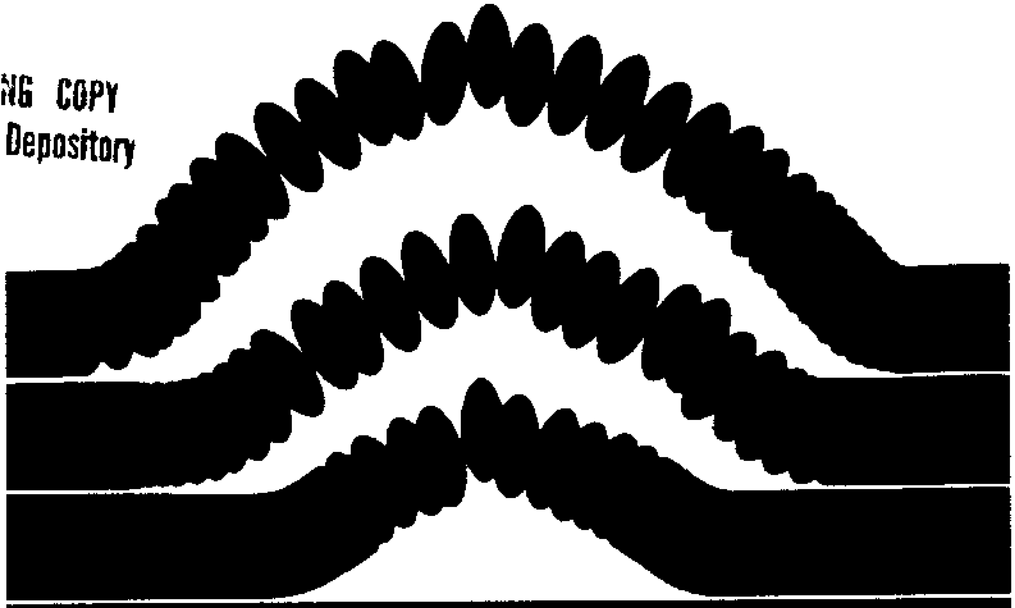

BLISTERING OF GLASS-REINFORCED PLASTIC MARINE MATERIALS: A REVIEW

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BLISTERING OF GLASS-REINFORCED PLASTIC MARINE MATERIALS: A REVIEW

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FOREWORD

The authors undertook this study on the suggestion of a local manufacturer and at the urgings of Neil Ross, of The University of Rhode Island Marine Advisory Service. The work has been financed by an initiation grant from The University of Rhode Island Sea Grant Office and a donation from the American Boat Builders Association; the space, equipment, and salaries were provided by the University's Department of Chemical Engineering. Information, samples, and encouragement came from a number of people in various aspects of the boating industry, including suppliers, builders and repairers, and boat owners.

INTRODUCTION

Blistering of glass-fiber-reinforced polyester plastics has received much attention in recent years, particularly in areas of commercial interest such as marine laminates and swimming pools. Various articles have appeared in popular yachting magazines referring to gel coat blistering as pox, measles, or osmotic blisters (1-8). One marine surveyor reports that 20 to 48% of all fiberglass vessels show some evidence of gel coat blistering (4). At least 52% of the boat owners in a recent survey reported blistering on 30% or less of the boat's hull, while 27% of the boat owners reported blistering on 70% of the boat (8). The incidence of blistering may be even higher when correlated with warmer waters and longer immersion times. Its occurrence is independent of the age and make of the boat (1). Gel coat blisters may appear randomly on the hull or they may cover a considerable area. They usually occur below the waterline, but field observations and discussions with boat owners and marina operators reveal that blisters may also occur above the waterline—in areas that are kept wet or as a result of water wicking through the laminate. Marine surveyors and U.S. Coast Guard experts have drawn special attention to the gel coat's protective role and the effect its deterioration may have on the structural integrity of the laminate (9,10).

Much has been written on the blistering of gel-coated laminates in the marine trade journals and in the technical literature. This review focuses primarily on the scientific literature and the technology of manufacturing processes.

BACKGROUND

The manufacture of composite materials involves many variables, and it is difficult to make generalizations concerning the performance of a laminate from all the available data. It has been reported that variability in the performance of a hand lay-up is due primarily to variation in materials and their formulation rather than process variables (11). Other studies indicate that variables in processing are important in preventing the initiation of blisters (for instance, proper laminating techniques to insure maximum glass wet-out and minimum void formation, uniform gel coat thickness, good spray techniques, correct mold room environment, proper mixing of resin with catalyst, and sufficiently cured resin) (12,13).

Data that focuses on a relationship between blistering and the various parameters involved in the manufacturing process are becoming available in the literature. The differences in severity, appearance, and location of blisters suggest the complex nature of the interactions of many variables. It is likely that an interaction of variables in materials and processes plays a role in the performance of the final product.

NATURE OF COMPOSITE MATERIALS

Polyester resins cross-linked with styrene are used in the manufacture of fiberglass boats. An ester is an organic compound formed by the reaction of acid and alcohol. If a long chainlike molecule is formed by continuous reaction of acid and alcohol, the polymer is known as a polyester. In marine resins, orthophthalic and/or isophthalic acids are used. Glycols are the alcohols commonly used. This reaction results in a viscous liquid resin, which then is cross-linked with styrene, to form chemical bonds that link the polyester chains to one another and become a solid matrix. This final reaction, called curing, produces an insoluble, infusible, impact-resistant material (14). These materials are used as the base for gel coats and laminates.

The gel coat is a 15-20 mil mineral-filled, pigmented, non-reinforced layer of resin, which is normally applied to the mold in layers with a spray gun and provides a smooth surface for mold release of the laminate when the hull is completed (15). This coating functions as a cosmetic finish, since it provides a smooth, colorful, glossy surface over the underlying fiberglass network (16), and it also serves as a protective coating for the glass-reinforced laminated hull, to reduce water absorption and its effects as well as to reduce impact stresses (12,17-19). Ideally, it should require little maintenance.

The laminate contains reinforcement to impart high strength, stiffness, and resistance to mechanical stress. Properties of both the gel coat and the laminate can be modified by chemical formulation, glass reinforcement, cure, and other factors (20,21). Recent studies indicate that these modifications can influence the rate and extent of blistering (11,12,18,22-24).

FABRICATION METHODS

Fabrication techniques, which include mold conditions and preparation, gel coat application, and laminating procedures, can contribute to blistering of a gel-coated laminate. Implications of these parameters will be covered in more detail as part of the general discussion.

The need for increases in production rate, ease of maintenance, and the reduction of styrene evaporation has resulted in the development of various types of spray equipment for the application of gel coat and laminating resins (13). These require specific amounts of catalyzed resin to be dispensed to the mold surface with minimum porosity.

Generally, dual-feed spray nozzles with the catalyst and resin mixing outside the nozzle are used for most glass-reinforced plastic (GRP) applications. These spray systems may dispense resin by air or by airless atomization. Some of the problems encountered with air atomization--such as overspray, release of solvent, catalyst and styrene fumes, and the tendency to drive air into the resin--are minimized with airless spray equipment. However, even airless equipment can cause porosity and resin separation (25,26). A porous structure provides sites for the collection of water. Success of the spraying method depends upon proper catalyst level and adequate mixing of catalyst with resin.

Time of application of subsequent layers of gel coat resin and the laminating resin are important. Too much gelation of the previous layer will give poor adhesion and wetting-out of succeeding layers as well as decreases in chemical diffusion and bonding between resin components (27,28). If the next layer is applied too soon, the resulting composite may overheat.

The temperature and humidity of the working area are important considerations in the preparation of a laminate. As the temperature of the mold room changes, the amount of catalyst must be adjusted to achieve the required gel time. In addition, elevated temperatures increase styrene evaporation during and after lay-up. Loss of styrene is a cause of undercure in unsaturated polyester resins (29). Decreases in mold room temperatures can result in condensation on the mold surface, thereby leaving water pockets in the laminate which provide sites for the dissolution of various non-bound chemical species. Low mold room temperatures also decrease the viscosity of the resin. Adjustment is usually made by adding more solvent (styrene).

Air or oxygen can cause cure inhibition. Preferential reaction of free radicals with oxygen instead of styrene depletes the concentration of free radicals needed for copolymerization (21). This problem has been overcome by modifying the resin with additives such as paraffin wax (30). The wax migrates to the surface and forms a protective layer on the surface. The wax may also migrate to the resin-glass interface and affect the adhesion of the resin and glass (21).

Another factor important in fabrication procedures is mold preparation. An aqueous mold release agent is more likely to retard cure than one containing wax (22). This causes an increase in blistering, probably due to the formation of an aqueous solution of non-reacted constituents in the resin, resulting in poor cross-linking.

TEST METHODS

The success of GRP application systems is to some extent due to how well test results are interpreted and to the practical experience of manufacturers. Any evaluation of the testing of a composite material should include the effects of processing, particularly since laminates used for testing are "perfect" laminates and may not represent an actual fabricated part.

Generalizations from data are usually difficult to make due to the wide variation in test methods, cure cycles, and types, amounts, and composition of glass, resin, and other additives. In addition, the lifetime of any GRP structure cannot be based on the results of any of the following test methods without consideration of the proper manufacturing and processing methods.

The standard exotherm curve is a technique used to assess the cure rate and exothermic behavior of various resin systems (31,32). This test follows the physical and chemical changes occurring in the polyester during polymerization with variation in concentration of catalyst, initiators, promoters, and fillers, and can gauge the effect changes in formulation have on the performance of the resin. The test is useful in establishing quality control of the resin system, since the variation of exotherm temperature with time can be represented graphically.

Another test used to evaluate GRP is based on immersion of the material in an aggressive environment at high temperatures to accelerate the blister formation (33). This test method may cause appreciable "post-curing" of test laminates by changing the amount of cure, thus leading to errors in interpretation of test results. Studies have shown that the 100-hour boil test alters the physical properties of the resin and thus does not give results consistent with actual performance (17). Accelerated testing may be performed up to about 65°C without inducing chemical decomposition and temperature-related defects which occur above the softening point.

The Barcol hardness test is used to check the properties of a gel-coated laminate GRP. Although it is not very precise, it is a simple technique that can be used to measure surface hardness and to estimate the degree of cure of the laminate (29,34).

Other test methods that can be used to show a rel tionship between cure and resin formulation include dynamic mechanical analysis, refractive index, spectroscopic measurements, differential scanning calorimetry, velocity and attenuation of ultrasonic waves, resistivity measurements, and Young's modulus (35,36). These techniques, used mainly for experimental and research purposes, often aid in the determination of the performance of a test gel coat/fiberglass laminate.

THE MECHANISM OF BLISTER FORMATION

Blisters that occur in gel-coated marine polyester laminates are the result of a series of events. The causes are complex and not fully understood. Basically, there are three steps in blister formation:

1. Water permeates into the laminate.
2. Water-soluble components in the resin are dissolved in this water and are concentrated in cracks or voids in the laminate, creating an osmotic center.
3. More water is drawn into the laminate through osmosis, creating a localized pressure. The solution in the osmotic center hydrolyses the resin, resulting in an increase in water-soluble materials, which then draw more water into the laminate and increase the pressure.

Virtually all polymers absorb water. The amount and rate of water absorption is determined by the chemical nature and structure of the polymer. Water molecules are absorbed by the polymer and travel throughout the polymer matrix by a diffusion process. The permeation rate is inversely proportional to film thickness (23,27,42). The water accommodated in the polymer matrix causes an initial increase in volume, or swelling, until the structure reaches saturation. The water also may accumulate in pores or voids. In resin-starved areas, water traveling along the dry fiberglass packets by capillary action is referred to as wicking. As the water permeates into the resin, a limited amount of the smaller non-bound water-soluble constituents of the polymer are dissolved in the water to form a solution. This mechanism permits leaching of some low molecular weight species from the resin, while the remainder is permanently trapped in the polymer (43,44). Hydrolysis of water-soluble components of the glass and resin further increases the concentration of the solution in certain areas. As the concentration of the ions or soluble molecules in the voids increases over the concentration in the surrounding water, more water will be drawn into the area through osmosis. This phenomenon, defined as the transport of a fluid across a semi-permeable membrane, occurs when a gradient in chemical potential exists. If enough pressure builds up, the gel coat will blister or crack, depending on its mechanical properties (23,37,43).

A study of laminate cross-sections reveals that blisters may occur in the laminate, the gel coat, or at the interface (45). Components of blister fluids include acetic acid and other organic acids, glycols, metal ions, binders, and products associated with the catalyst, accelerator, and plasticizer (22,37,45).

Recently, it has been shown that the presence of free glycol in the laminate has a major effect on blistering (22,37). The free glycol may be present from the outset due to incomplete utilization during resin synthesis (43).

RESINS

Many resin systems have been studied. It has been demonstrated that improvement in resin formulation and reinforcement can control the water permeability in a gel-coated laminate. Existing and new resins with improved hydrophylic stability are currently being investigated (18,46,47). The major resins used in the marine industry are unsaturated polyester resins. They consist of an unsaturated acid, a saturated acid, and a glycol with an unsaturated monomer (styrene) to work as a solvent and for cross-linking to form the three-dimensional solid structure. Base polyesters are produced by the polycondensation reaction of phthalic and maleic anhydride with one or more glycols (e.g., propylene and diethylene glycol). The chemistry and manufacturing processes of resins have been studied and reported on in detail elsewhere (14,31,49-52).

Polyester resins are solutions containing many components. The final properties depend on how these components join to form the final solid. Even when their formulations are apparently identical the components may join in different ways, resulting in different properties. Some very important parameters including the ratio and type of constituents, average molecular weight (which is determined by the size distribution), length of polyester chain, type of end groups, and distribution of unsaturated sites along the polyester chain determine the properties of the final cured product. However, while change in composition (e.g., styrene content and glycol components) can improve hardness, frequently it is at the expense of other desirable properties such as flexural and tensile strength (21).

For the manufacture of large fabricated products, polyester resins, particularly the orthophthalic and isophthalic resins, have become the most widely used. Some studies indicate that there is no significant difference in a gel coat made with orthophthalic resin or isophthalic resin (12,24). Other studies indicate an isophthalic gel coat is far more blister-resistant than an orthophthalic gel coat, but this is not always reflected in the data. Several studies indicate that an isophthalic resin used in the laminate improved water resistance compared with an orthophthalic resin (12,14,18,43,53). The following discussion will attempt an explanation of the differences in the conclusions of these studies.

The molecular structure of the units that make up the different types of polyester confer various degrees of hydrolytic stability to the set polymer. Also the way the units are arranged next to one another affects hydrolytic stability, an effect called steric hindrance. There are three types of phthalic acid. They all have the same chemical composition, but their molecular structure differs. Figure 1 shows the three structures.

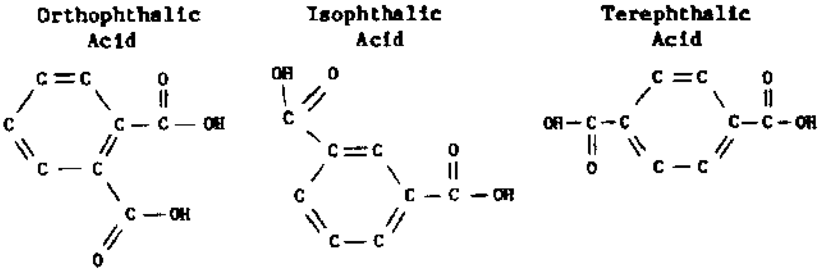

Figure 1. Structure of phthalic acids
(e) indicates the position of ester linkages

The ester linkages formed at 120° are more stable than those formed at 60°. Using isophthalic acid instead of orthophthalic acid slows down hydrolysis due to changes in steric effects (30). In other words, easily hydrolyzable ester linkages are shielded by pendant methyl groups. Vinyl ester resins show better resistance to water penetration and increased resistance to hydrolysis.

Several reasons for the increased resistance are given. First, unreacted vinyl groups at the end of the molecule are very reactive. This causes the polymer chain to cross-link more completely and cure more rapidly. Second, vinyl ester resins have a minimal number of ester groups per unit molecular weight. This is in contrast to polyester resins, where ester linkages are part of the repeating unit. Third, improved wetting and bonding of glass fibers by the interaction of hydroxyl groups on the glass and resin imparts higher strength to laminates. Fourth, the epoxy resin backbone is stable in many chemical environments. It also allows the control of molecular weight necessary for low viscosity, and the epoxy ester bond provides excellent chemical resistance. Finally, methyl groups shield susceptible ester linkages from hydrolytic attack (52).

Other groups of resins such as the epoxides and Bisphenol-A polyesters exhibit good resistance to water penetration for similar reasons. In comparison studies, epoxides have been shown to have lower permeability than polyesters because osmotic centers are rarely present (37). These osmotic centers, or disc cracks, are produced during water immersion, and the mechanism of their formation has been studied in detail (38,39). Briefly, these cracks arise from the interaction of water-soluble constituents with water. Pockets of pressure are generated and cracks propagate. This is partly why GRP suffer a loss in mechanical strength upon exposure to water. Bisphenol-A polyesters also show better resistance to water penetration than isophthalic polyester (42). Cost, ease of handling, mechanical and physical properties are some variables that may affect the choice of these resins for large fabricated products (31).

The alcohol components of the unsaturated polyester also affect the ability of the polyester to absorb water. The amount and type of glycol has been shown to influence blistering. Excess glycols added to unsaturated polyesters during their manufacture are employed to adjust viscosity, reduce acid number, and compensate for any losses during the polymerization reaction. This results in the presence of free glycol in a cured laminate, which, as already mentioned, has been shown to enhance blistering (22,34). Another factor that plays a role in affecting water absorption is the type of glycol (21). Improvement in blister resistance is attained when resins are formulated with neopentyl glycol (NPG) (12,17). The symmetrical structure of this molecule yields a "solid" polyester compound at room temperature. This increases the crystalline component of the resin and enhances the hydrolytic stability of the polymer. It has been established that highly crystalline polymers are less permeable than amorphous polymers. This is because the physical structure in crystalline regions involves interchain bonding and resists the penetration of liquids (54).

To date, there are several other glycol compounds available for use in unsaturated polyester systems. These include TMPD (2,2,4-Trimethyl-1,3-Pentanediol) and CHMD (1:4 Cyclohexane Dimethanol). These possess excellent hydrolytic stability and are suitable for a wide range of applications. However, there is little evidence available that they are being used to any significant extent in marine applications.

The acid components other than the phthalic group also affect water absorption. For example, maleic anhydride, used in the preparation of the polyester, exhibits lower water resistance than fumaric acid (21). Saturated acids with long aliphatic chains or aromatic acids with polar ester groups show better water resistance. Low acid values have an influence on water absorptivity and increase blister resistance. This may be due to lower numbers of hydrolyzable end groups, which will effectively lower the water permeation rate (22).

THE CURING MECHANISM

The unique factor in the fabrication of large structures is the cure or setting process. All resins, plastics, or polymers may be classified as thermosetting or thermoplastic. Those that form rigid solids by cross-linking are known as thermosetting polymers because as they are heated more cross-links are formed and they become more rigid. Thermoplastics soften when heated and set again when cooled without undergoing a chemical change. The interrelationship between the curing mechanism, resin chemistry, and the final properties of the polyester resin laminate is very important. The nature of catalytic action, which triggers the cross-linking mechanism, the amount of cross-linking, and uniformity of cross-link density of the cured resin are determined by their formulations (55,56). Steps in the curing reaction of a particular resin/catalyst system are typified by an exotherm curve. Polyester resins are cured by a free radical copolymerization reaction which is initiated by a catalyst-accelerator system at room temperature. Under normal cure conditions, the full properties of the resin can be realized at 92-95% of cure (31).

Ideally, all unsaturated sites (reaction sites for cross-linking) in the polyester resins should react completely with the cross-linking agent. In practice, this is difficult to achieve. Final hardening of a resin may take days or weeks depending on temperature and other conditions. From the manufacturing/process viewpoint, it is desirable to reduce cure time, thus reducing the cost of molding processes and increasing productivity.

The failure of unsaturated sites to react completely causes unreacted materials from the gel coat and lay-up resins to contribute to the osmotic process by being free to dissolve in water permeating into the resin. The amount of cross-linking depends on the ratio of styrene to unsaturated sites and the number of unsaturated sites in the polyester. Water absorption usually decreases with increase in styrene content due to its low solubility in water (21,57). Free styrene does not present an immediate concern in its contribution to osmosis. However, it may react with free radicals generated from the peroxide. These free radicals are present in the resin and reduce the supply needed to initiate cross-linking with the styrene (22,58).

Most of the laboratory studies use various post-cure methods. These range from long periods at low temperatures (e.g., 20°C for 28 days (22)) to higher temperatures for shorter periods (e.g., 40°C for 16 hours (12)). In some cases, a two-stage regime is used (e.g., two hours at 66°C and one hour at 93°C (24)). This treatment increases the degree of cross-linking. Since boats are not post-cured at elevated temperatures, post-cured specimens may have somewhat different properties than material produced in actual processing.

CATALYSTS AND PROMOTERS

Catalysts or initiators, and promoters or accelerators, are used to achieve rapid cure at room temperature for the manufacture of large fabricated parts. These compounds break down to form free radicals, which cause cross-linking. The selection depends on the user's application, and the rationale for selection has been reviewed by others (52,59).

Cross-linking of the polyester with styrene is brought about by the catalyst-promoter system. Poor mixing of these will lead to non-uniform properties in the cured state. The term "catalyst" as it is used by many in the industry is a misnomer. In the copolymerization reaction the catalyst must decompose to initiate the reaction, and therefore the term "initiator" is more exact and a better choice. However, since the term "catalyst" is so widely used, it will be the term employed here for the organic peroxides. Methyl ethyl ketone peroxide (MEKP) generally serves as the catalyst for room temperature cure of polyester resins. Changes in catalyst levels from 1 to 2% showed no effect on water absorptivity or the rate of blister formation (12,17). A comparison of catalysts shows that the rate of blistering with benzoyl peroxide (BPO) is higher than with MEKP. This is probably due either to BPO decomposing too quickly for the resin system or to the formation of a non-radical breakdown product. Both mechanisms deplete the availability of free radicals needed for cross-linking initiation (22,59).

Cobalt naphthenate is the promoter commonly used for organic peroxides and can be detrimental to effective cure when optimum levels are not employed. One reason for this is that cobalt has a tendency to form complexes with constituents in polyester resins such as styrene (22,60). As the concentration of cobalt increases with regard to the different amount of MEKP in an orthophthalic resin, the amount of cure measured by the Barcol hardness test decreases because the cobalt also reacts with free radicals and converts them to ions (52). This reduces free radical availability and affects the polyester cure (59). Thus, as the cobalt concentration changes, the MEKP concentration must be adjusted to maintain the desired cure characteristics.

The time and temperature of curing, in practice, can be varied by systematically varying the amount of promoter or catalyst in the system. As the temperature increases, less catalyst can be added to maintain the same cure rate. An excessive exotherm due to thickness of resin layers can cause evaporation of styrene, leading to volume changes, incomplete cross-linking, and residual internal strain (61).

REINFORCEMENT

In thermosetting resins, several types of glass reinforcement are used, including veil mats, chopped strand mats, woven roving cloth, and unidirectional fiber cloth. The manufacturing and technology of glass fibers has been described in detail in the literature (31,62,63). After the fibers are drawn, they are sized with a solution containing a coupling agent and a lubricating film. One end of the coupling agent bonds to the glass and the other is available for bonding to the resin. The lubricant allows the glass fibers to be easily woven and matted, preventing damage to the glass surface. Usually the size, lubricants, and finishes used in the early manufacturing processes are removed before the binder is applied. The binder is used to hold the mats and cloths together for ease of handling during lay-up.

It has been demonstrated that the variation in type and amount of glass reinforcement affects the resistance to blistering of a laminate. Even though the rates of water permeation decrease as glass content increases the degradation of a reinforced plastic may occur faster, since more sites on the glass surface are available for hydrolytic attack (42). Studies indicate that a surface veil mat applied between the gel coat and laminate reduces the incidence of blistering (23). A possible reason for this is that veil mats generally contain little or no binder and provide a transition region, a resin-rich area, where interaction of water with glass fibers is minimized. It may also be related to the fact that the resin-rich veil mat acts as an added coating to decrease the rate at which water permeates into the laminate.

The importance of the surface chemistry of the glass-resin interface has a profound influence on the properties of a reinforced plastic. The need for complete wetting of the glass surface by the resin is desirable for several reasons. The surface treatment provides an adsorbed hydrophobic film on the glass fibers which provides protection from chemical attack, insures good adhesion, minimizes the work needed to remove air bubbles during rolling out, affects the wet-out rate, which is important for rapid mold turnover, and minimizes the number of resin-poor regions in the laminate by surface chemical reaction.

The type of surface treatment used, whether binders or sizing, coupling agents, film formers, plasticizers, or others, depends on the requirements of the molding process. Studies have shown that surface treatment coatings play a role in blistering (12,22,37). Two kinds of binders are commonly used. These are polyester powder-bound mats and plasticized polyvinyl acetate (PVA) emulsion-bound mats; both kinds of mats can have either fast or slow wet-out rates. The binder enables the glass fiber to be completely wet by the resin, thereby making it easier to produce a void-free lay-up during wetting of the glass by resin. A comparison of slow wet-out emulsion-bound mats with fast wet-out emulsion-bound mats showed little difference in blistering (12).

Due to the variation and presence of chemical additives in binders, it is difficult to make generalizations about the types of emulsions that may affect the properties of the glass and influence blistering. In one study of gel-coated laminates, powder-bound mats performed better than emulsion-bound, but it depended on the type of resin (12). Another study comparing PVA emulsion-bound mats/PVA size with polyester powder-bound mat/powder-bound size showed that PVA mats encouraged blistering due to hydrolysis of the PVA binder (22).

In the presence of water, sites at exposed glass surfaces and traces of organic materials left from surface treatment of glass are susceptible to interdiffusion and reaction with resin components and may contribute to the osmotic process (37). It has been demonstrated that the components of resin--polyester, monomer, and catalyst--prefer adsorbing to the glass surface independently rather than reacting in the cross-linking mechanism (64). While many studies contend that resin-starved areas contribute to osmosis, it has been shown that poor impregnation did not increase the blistering. These defects can easily allow the diffusion of water in and out of the laminate so that no concentrated solution can form to contribute to osmosis (22).

In resin-starved areas, water may be transported along the glass resin interface by capillary action. This phenomenon, called wicking, depends on the nature of the resin and the type of glass finish. Wicking permits water to travel to areas that are not accessible through normal diffusion processes and may be one of the causes of blisters above the waterline. However, no increase in blistering was observed in test panels with poor impregnation which were immersed in distilled water at elevated temperatures (22).

ADDITIVES

Another factor that affects the permeability of the resin is the use of additives such as pigments, thickeners, and fillers; these are important in the formulation of a resin. Other additives such as inhibitors, stabilizers, plasticizers, and fire retardants serve an ancillary purpose and are used for the control of properties like weathering, storage, and viscosity (20,30,31,65), and may also affect permeability. Care must be taken in the selection of additives so that they do not interfere with the glass reinforcement and the resin-initiator-catalyst system. Few studies show the effect of all of these additives on the blister resistance of gel-coated laminates.

Although several studies have examined the effect of pigment on blistering, the information appears to be contradictory. Pigment concentration and the nature of the carrier media used to blend the pigment are factors in blister formation. A comparison of results of the blister resistance of white-pigmented gel coats with clear gel coats showed no difference (12), while another study showed that an increase in the concentration of pigment improved blister resistance. This is thought to be due to an increase in the heat distortion temperature of the system (18). It has been found that blisters are produced at a faster rate by darker pigments (12,22), probably because some pigments are dispersed in a carrier media which may contain low molecular weight, water-soluble species. However, one of these studies showed that blisters were produced at a faster rate even without a carrier (22).

There is little comprehensive evaluation of the effect of fillers on blister resistance in the literature. The most common fillers used in unsaturated polyester resins are relatively simple inorganic compounds such as clays, calcium carbonate, and silica (65). For the most part, they tend to be hygroscopic. Fillers provide desirable thixotropic properties to the resin, improve the mechanical and physical properties of the laminate, and are economical to use. The primary effect of fillers in a resin is to modify the exotherm temperature during cure (66). This tends to reduce shrinkage of resin during cure and reduces surface crazing. In spite of reduction in crazing, blisters are still produced. Unfortunately, fillers in appreciable quantities can increase water absorption. Another effect of fillers is the shrinkage of resin away from the filler, which can occur after repeated heating and cooling of the laminate system during cure. This may result in higher shrinkage, voids along interfaces, and cracking of the resin-rich areas (67).

There are several groups of inhibitors used to prevent premature curing. Discussions in detail of these can be found in the literature (31). The type and amount of inhibitor used affect the rate and degree of cure, and may also influence blistering. One study suggests that contamination of gel coat resin with inhibitor leads to excess styrene evaporation by retarding the cure (22).

Several studies have suggested the presence of plasticizers in blister fluids (12,68,69). An evaluation of the effects of plasticizers on the blistering of laminates has not been made. However, inappropriate application and use of plasticizers could accentuate the blistering problem.

Modification of the polyester with flame retardants also can affect the viscosity, weathering, and strength of the polyester and, possibly, could increase blister formation. Flame-retardant polyester formulations have been reviewed (70-72). Flame-resistant polyester resins are not normally used in the manufacture of boat hulls, since their effects may produce deleterious results in product performance as well as an increase in cost and a reduced resistance to aging (21).

OTHER CONSIDERATIONS

The retention of mechanical properties after immersion in an aqueous environment is also important. The same factors that affect the permeability in the resin/laminate system--i.e., resin type, glass fiber, cure cycles--also control the corrosion of a GRP under stress-strain conditions. It has been established that immersion in water of a GRP leads to a decline in strength with time (73). In fact, the application of stress encountered in service may accelerate deterioration of the laminate. In response to the net effect of shrinkage and swelling due to water absorption, a gradual debonding of the resin-to-fiber bond may occur. The mode of failure under these conditions has been examined by several authors (52,61,74-76).

Under stress-strain conditions, the integrity of the gel coat is extremely important. Tests have shown that an intact gel coat can delay stress corrosion of a laminate (77). Another study suggests that the strain-corrosion failure of a laminate can be prevented without any need for specially formulated resins if a gel coat thickness of 1-2 mm is used (78).

CONCLUDING REMARKS

The many variables involved in the manufacture of GRP boats make it very difficult to pinpoint the causes of blistering. The concerns that have been expressed depend on a person's perspective. The resin manufacturers are providing formulations that have the chemical, physical, and mechanical properties needed in fabrication; the individual suppliers are responding to the specifications provided by the boat manufacturer; while the builders want to produce a well-made vessel as economically as possible. The boat owner is looking for a long-lived low-maintenance vessel, and the boat repairers need a rapid, inexpensive, permanent method to repair blistered boats. Although the resin manufacturers have been developing new resins and new formulation, very little basic research has been done on the mechanisms of blistering and on the effects of day-to-day variations in the manufacturing process. There are many examples of boats built by the same yard with the same material and deployed in the same area having different blister susceptibility. In some cases, different areas of hull in the same boat react differently. Frequently, research data on different formulation do indicate some trend. However, the data also shows large differences in blister resistance among similar test specimens.

In order to permit the development of laminates that are more blister-resistant, it is necessary to better understand the mechanism of blistering. More studies are needed on the effects of processing variables. In addition, physical studies should be conducted on various stages of blisters grown under laboratory conditions as well as those occurring in the field.

There is reasonable evidence that proper selection of materials and procedures can produce boats with better blister resistance. However, there is a need for careful specifications both of material and process parameters as well as good testing methods. The British Plastics Federation has provided a good set of guidelines based on supporting experimental evidence (79). The American Bureau of Shipping has also established rules, but they differ from the BPF standards in specifying manufacturing and processing restrictions (80). In most cases, the ABS refers the builder to the standards and specifications recommended by the manufacturers or suppliers. Even though good manufacturing practices are recommended, implementation is not always consistent. In light of all the available evidence about the variables that cause blistering in GRP, it seems well advised that the industry itself formulate a set of standards.

Once the boat has blistered, the problem resides with the boat owners and repairers. In addition to the problems of material selection, the repairers have to select the appropriate techniques for preparing the hull and for applying the patching material. Description of blister types, assessment of their significance on the hull's structural integrity, and recommendations of appropriate remedial action to be taken have been discussed by the British Plastics Federation (81). However, methods should be developed for earlier detection of the problem, and studies should be conducted on what effects surface preparation and methods of applying the new coating material have on the reoccurrance of blisters.

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