

NUTS & BOLTS

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Hydrolysis of Fiberglass

Hardly a week goes by without our being asked to do a failure analysis of something made of fiberglass. The failure may be an industrial tank, piping, a yacht hull, a swimming pool, or a water tank in an RV. This issue of "Nuts and Bolts" addresses the failure called "hydrolysis", as well as a very different kind of failure due to leaching of a constituent in the fiberglass' resin. We hope neither of these happens to you, especially since the insurance industry usually classifies these as "wear and tear" failures so they are not often covered.

Overview of the Chemistry

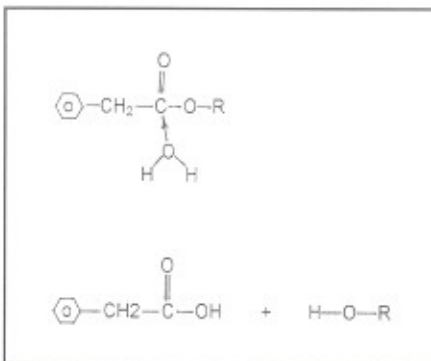
All of the different molecules that can be used to make up the various polyester-based fiberglass resins are subject to deterioration by hydrolysis. For hydrolysis to occur, water as liquid or vapor must be present. The reaction is markedly accelerated by elevated temperatures. In the hydrolysis reaction, water molecules break up the resin molecules, leaving an organic acid

of varying acidity depending on the particular resin and a mixture of molecules of water, alcohols, and glycols. After a period of time, only the heavier alcohols and the glycol will remain.

Technical Background

An ester molecule has the following structure:

The hexagon is a ring-type group such as a benzene. In polyester, R is a carbon and hydrogen chain-type group. In vinyl ester, R is a vinyl chain. When these esters undergo hydrolysis, a water molecule attacks the bond between the central carbon atom and the adjacent single-bonded oxygen atom. The water molecule dissociates into a hydrogen atom and an OH pair. The OH pair takes the



NHML Acquires DSC

A Differential Scanning Calorimeter (DSC) is an instrument which accurately measures the heat absorbed or given off from a sample as a function of temperature. Such thermal parameters as the Glass Transition Temperature (TG) (which is the temperature at which a glassy material begins to flow), the melting temperature, and the enthalpy of melting can all be measured by DSC. Our main interest will be the melting temperatures and glass transitions of polymer samples, however, the DSC can measure thermal properties for crystalline organic compounds and liquids as well. DSC data is most often used in conjunction with TGA data (which gives weight loss as a function of temperature) and FTIR data, which provides the identity of a polymer sample. Such thermal parameters as the glass transition, melting point, and decomposition temperature are useful to engineers who must select polymers to withstand a given thermal environment.

Hydrol of Fiberglass, Cont'd

place of the original single-bonded oxygen while the hydrogen joins the O-R to become H-O-R. The C = O pair is referred to as a carbonyl.

The OH group's electrons are somewhat mobile within the molecule, wandering between the OH and the double-bonded oxygen. If, in a particular molecule, the electrons divide their time between the OH pair and the double-bonded oxygen, then the molecule is a weak organic acid. Should the bonding electrons spend much of their time away from the OH pair, the resulting electron deficiency makes the molecule into a stronger organic acid. The degree of acidity is increased by the presence of nearby "electron withdrawing" atoms or groups. For example, chlorine is a strongly electronegative atom that increases the acidity through "electron withdrawing" from the carbonyl. In the particular case of a hydrolyzed polyester, the acid product is carboxylic acid.

The molecule that is cut loose during hydrolysis could be a water molecule, an

alcohol, or a glycol. After hydrolysis has occurred, the water and lighter alcohols will be lost by evaporation. Heavier alcohols and glycols do not volatilize but will accumulate.

Hydrolysis Failures

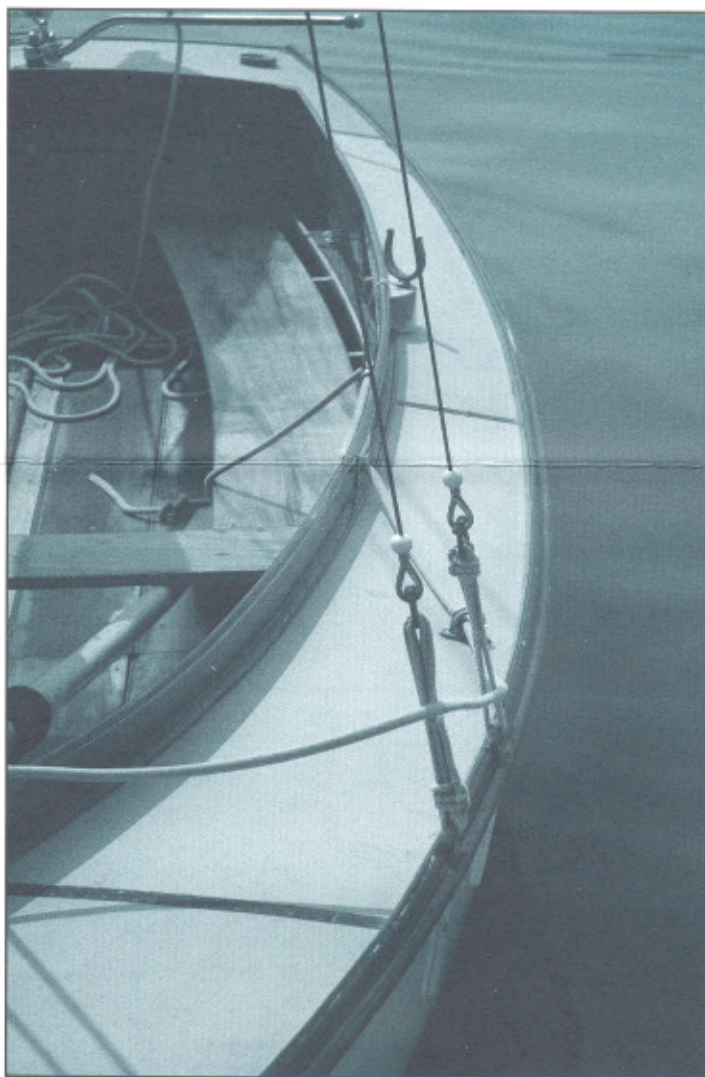
Delamination, blistering, and bleeding are the common failures. After having set, the original polyester molecules are immobile. After hydrolysis, the new molecules have some mobility and also occupy a greater volume than the polyester molecules from which they came. The result

is internal pressure. The pressure, along with the natural mobility of the molecules, causes them to fill any voids in the fiberglass, including the pinhole porosity that is always present. If they can't escape to the surface fast enough, and if there are any deficiencies in the composite, then blistering and delamination are common results.

The first requirement for hydrolysis is water absorption. A dry sailed boat or an intermittently used tank will probably not fail by hydrolysis.

A swimming pool that is always filled, a yacht that is always afloat, or a tank that is usually filled are candidates for eventual failure. Because elevated temperatures accelerate the hydrolysis reaction, both delamination and blistering are more widespread in southern climes. A tank holding warm water is especially at risk.

Fiberglass structures that are well sealed by their gel coat or another surface coating may suffer severe blistering since the byproducts of the hydrolysis reaction may not be able to escape as fast as they form. A swimming



Hydrol of Fiberglass, Cont'd

pool or a hot tub that has a good gel coat on one side only may not blister or delaminate since the byproducts may be able to escape out the back door. A yacht or a tank that is well sealed on both sides is more likely to develop the internal pressure that is the precursor to structural failure.

When we encounter widespread delamination it is often in deficient layups that have insufficient strength to withstand the internal pressure. Analyzing these layups, we may find high resin/glass ratios, resin pockets and porosity.

Bleeding is another failure. Even the best fiberglass composites have at least a few pinholes where the reaction products concentrate. Sanding the fiberglass in preparation for refinishing may break into these pinholes. They release a fluid having an acidic smell along with the color of the glycol component, often a green or blue. When we recently analyzed a smelly, blue goo bleeding from the pinholes on a yacht undergoing resurfacing, we found it to be predominantly the carboxylic acid that forms during failure by hydrolysis.

Leaching

When organic liquids are stored in fiberglass tanks or

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run through fiberglass piping, the possibility is always present that the stored liquid may dissolve some constituent out of the fiberglass. We have analyzed gasoline stored in fiberglass and found some of the lightest molecules in the gasoline diffusing out of the gasoline and into the fiberglass. At the same time, some heavy molecules were dissolving out of the fiberglass and into the gasoline.

Only recently has ethanol been added to gasolines, with 10% a common amount. The ethanol in the gas can dissolve some molecules in the fiberglass that always used to stay put. Fortunately, most of these molecules burn right along with the gasoline so we never notice that they are present. Unfortunately, the 10% ethanol in E10 gasoline is picking up some phthalates in older fiberglass. The phthalates are particularly stable molecules that seem to

be traveling through an engine's induction system as extremely fine droplets. When these droplets reach the hot back side of each intake valve they stick and, instead of burning, they decompose into a heavy deposit of black goo. (We can tell you the chemistry of the goo, but you probably wouldn't be interested!) That goo can cause the valve to hang up, followed by the piston hitting it on the next revolution, resulting in very bad things happening immediately in the engine.

So far we have only seen the problem in some pre-1980 yacht tanks. We are keeping our fingers crossed for the E10, the E85 that is just beginning to be introduced, and who knows what molecules that are going to be appearing in biodiesel.

For an article on the chemistry of blisters on boat hulls see

http://www.daviscoltd.com/nams/Documents/Blister_Report.html

For an article that covers how to cope with hydrolysis of boat hulls, see

<http://www.zahnisers.com/repair/blister/blister1.htm>



Our Philosophy

New Hampshire Materials Laboratory has one goal—to help you solve your technical problems at a reasonable cost. Tests help, but are not always enough. Our team of dedicated and experienced professionals have the skills and the backup facilities to serve in the following:

- **Failure Analysis**
- **Material Certification/Compliance**
- **New Product Testing**
- **Mechanical Properties**
- **Tensile/Compression Testing**
- **Heat Treat Problems/Verification**
- **Reverse Engineering**
- **Weld & Life Testing**
- **SEM & EDS**



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