Two-Phase Epoxy Systems for Composite Cored Boat Construction

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I. Abstract

Total emphasis has been placed on the mechanical properties of resins with little consideration of "toughness" properties. Properties of various boat resins are examined and related to historical changes in high performance boat hull construction. A quantitative concept of toughness is introduced which will allow resins to be evaluated on the basis of a balance of properties rather than on the basis of high mechanicals alone. Epoxy resin two-phase morphology is shown to be the best answer to achieving an optimum balance of properties with current raw materials. A designer who understands the concept of toughness and balances both the mechanical and toughness properties of the resin has an opportunity to develop lighter and stronger boat hulls that will out perform those currently being built.

II. Discussion

A. Historical Overview:

Early RP boats were of solid core construction using alternate layers of mat and woven roving laminated onto gel coat using polyester resins. Most boats produced today are built the same way as there have been few changes in the style of construction.

Solid laminates have poor stiffness to weight ratios. They are heavy due to their density. Technically, the best that can be said for boat hulls built using this method of construction is that they have good puncture resistance and are relatively maintenance free due to excessive weight and volume of materials used.

In the early Seventies several builders from California reasoned that if thin skinned surfboards built with RP, balsa and later foam cores could handle the abuse they get then surely a sailboat could be built in similar fashion and stand up to the punishment it gets. And, they felt, a lightweight boat properly designed could get on the plane and move faster than a displacement boat.

Composite-cored construction started as a revolution. Few serious racing sailboats are built today using RP in any other method of construction. Furthermore, the matrix and fiber materials used today did not exist for boatbuilders then; and it was the pull of the "composite core" builder/sailors that brought them into use.

These early builders soon learned that mat and woven roving were not suitable for this method of construction. The search for new fibers was on and many builders began to look to the aerospace industry for them. Non-woven unidirectional S-glass was first used, and was rapidly followed by Kevlar and graphite unidirectional fabrics. These fabrics were initially used with polyester resins and builders began to seek improvements by using vinyl ester resins.

Vinyl ester resins have generally better mechanical properties than polyester resins. They have higher tensile, flexural, and compressive strengths along with higher moduli. Their adhesive properties are better and they have higher impact resistance. For the most part they withstand fatigue better. Wet strength retention is better as they are less subject to degradation by moisture.

Vinyl esters, although a general improvement, still have problems: Cures are often inconsistent, are oxygen inhibited, and will continue to crosslink (imbrittle) on U.V. exposure. Delamination, primarily due to low interlaminar fracture energies combined with chemically induced stress concentrations at the fiber/matrix interface because of resin shrinkage will occur. Adhesion to cores is still a problem – again as a result of resin shrinkage, low fracture energy and inability to distribute stress. Vinyl esters have no peel strength on a metal/metal bond. Shelf life is poor and cures are often too fast for vacuum bagging, a construction technique primarily used to raise fiber volume and reduce void content. While they are "tougher" than polyesters, they are not tough enough by at least an order of magnitude. Finally, the "styrene stench" with accompanying flammability and toxic hazard is ever present.

As a result of these limitations several builders turned to epoxy resins. Many of the problems inherent with vinyl ester resins were overcome. However, despite their problem solving versatility, the epoxy resins brought in a fresh new set all of their own: These resins when cured with hardeners at room temperature either have relatively good mechanical properties and heat distortion resistance but are very brittle or else they have good impact strength by relatively poor mechanical properties and heat distortion resistance. Indeed, it is difficult to get the proper "balance of properties" in a single phase, room temperature cured, epoxy resin when the product requires some degree of elevated temperature strength. As a result of builders not understanding this

tradeoff, the first epoxy matrix boats generally were of poor quality.

Again, a good part of the answer lay with the aerospace industry, which had achieved an excellent balance of properties through the added criteria of fracture toughness and two-phase epoxy morphology. This technology has been combined with glass, Kevlar, and graphite fiber in pre-preg form and is utilized in the largest composite uses for commercial aircraft.

B. Toughness Properties

"Mechanicals" are those properties characteristic of stress/strain relationships within a resin or laminate. As such, they include tensile, compressive, and flexural strengths along with their respective moduli. These properties are well understood by builders and designers alike. They are conceptually easy to understand as they pertain to strength. Various resins are often evaluated by comparing their respective mechanicals. Generally, the basis of comparison is "stronger equals better".

Toughness properties are not as well understood. They have to do with interlaminar strengths such as peel and shear, fatigue resistance, impact strength, and fracture behavior. These all point to the durability of the resin and resistance to delamination of the laminate. That is, a tougher resin would be expected to have a longer service life than one that is less tough, mechanicals being equal. The tougher resin could be expected to be put through many more stress/strain cycles with lower loss of initial mechanical properties than the less tough resin and resist microcracking and interfacial failure.

Until recently, there has been no simple quantitative measure of these properties in an all encompassing way that would allow various resins to be compared on a meaningful basis. However, several years ago a concept of interlaminar fracture toughness was developed that can be used to compare various reinforced plastics using different resins. The use of this tool will allow naval architects and engineers to better design laminates for their intended use.

The toughness of a laminate is the critical value of the strain energy release rate, G, required to cause a delamination crack to grow under steady state conditions. Physically, it represents the rate of energy lost per unit of interlaminar surface area created when delamination occurs. In practical terms it is the ability of the laminate to absorb and dissipate strain energy in the area of a crack.

This concept of growing a crack gives rise to a companion notion of the stress intensity required to initiate delamination in the area of a crack – the fracture toughness of the laminate, K. Physically, this is a measure of the stress required to advance a crack of known length in a structure of specific geometry.

A laminate with higher K and G values is tougher than one with lower values simply because it takes more energy to begin delamination and, once begun, to spread the delamination.

Resistance to delamination is crucial for the skins of composite boat hulls using balsa or foam cores. In fact, almost all of the stress on the boat hull is concentrated in the skins. The primary purpose of the core is to separate the skins. Stiffness is achieved through this separation much in the same way that an I beam works. Skin delamination usually initiates a compression failure in the outer plies causing the core to fail leading to catastrophic failure of the entire structure.

In addition to measuring laminate toughness, K and G measurements can also be performed on a neat resin. Comparative data can then be used to predict which resin will produce a tougher laminate. A resin with higher K and G values will produce a laminate with higher values although the correlation is not always linear. The quantitative relationship is not fully understood at this time; although empirical relationships have been established where composites with tough matrices have about one third the value of the neat resin.

C. Balancing Mechanical and Toughness Properties

The various moduli (tensile, flexural, and compressive) calculated for the stress/strain relationships in mechanical properties are all roughly equal to each other for any given resin. Thus, an average of the three moduli might be used when comparing different resins. A plot of this average could be shown on the vertical scale of a graph as in figure 1 with modulus increasing toward the top.

There would, of course, be a great deal of overlapping of various resin types depending on the specific formulation of the particular resin within the type (epoxy, vinyl ester, etc.). Nevertheless, there is some lower limit of modulus below which a designer would not select a boat hull resin. A resin selected below this threshold limit will not have adequate stiffness and strength for the maximum service temperature expected. Use above this temperature will result in compression or buckling failure.

This does not necessarily mean that in comparing resins with moduli above this limit that the higher modulus resin is the better resin. If a resin is, for example, stiff enough then having it even stiffer most likely is unnecessary and could be detrimental to other properties. The same can be said for any of the other mechanical properties.

Since the toughness of a resin can be measured through the critical strain energy release rate, G, it is fair to measure the modulus off the same resin and plot it along with the G value on the same graph. The G value, therefore, becomes the horizontal line of the graph in figure 1 with toughness increasing toward the right.

Obviously, the very best resin would fall in the upper right hand corner of the graph. That is, it would have the highest mechanical properties as well as the highest toughness properties. In general, these are inverse relationships with polymer chemists and engineers continually trying to design new matrix concepts to achieve a quantum leap towards the upper right hand corner. Currently no such breakthrough has been made. But as long as a resin has adequate mechanicals for the intended service then, clearly, the best resin in any comparison will be the toughest resin even if the other resin has better mechanicals.

It will be best simply because toughness will help protect it against the degradation of its fully adequate mechanical properties. On the other hand the less tough resin might lose

initially superior mechanical properties. Clearly then, selecting a resin solely on the basis of high mechanicals with no consideration of toughness is a mistake the informed designer will avoid. Ignoring the toughness of a boat resin will either lead to costly over design or, worse yet, to a shortened service life through delamination failure which will be matrix or interface initiated.

Indeed, as the aerospace industry has discovered, this is the case: Composite laminates are matrix limited because they are not tough enough not because they are not strong enough. The same would be true of laminates used in composite boat hulls. These hulls will always be made with voids, flaws and foreign matter present in the laminates. These imperfections will cause stress concentrations, which must grow into cracks under service conditions. It is the toughness of the resin used that prevents such growth: or, in the case of the less tough resin, allows it.

It is informative to consider the relationship between average moduli and toughness in specific resin formulations. For example, two epoxy resin formulations identical except for the addition of a material to increase toughness will show a slight decrease in moduli as toughness significantly increases. This is shown in figure 1. As long as mechanicals are higher than the threshold line with a built in allowance for safety, then toughness properties should guide the designer to the proper resin choice.

The scanning electron micrograph (SEM) in figure 2 shows a delamination crack in a laminate made from an epoxy resin with low toughness but otherwise excellent mechanicals. A wedge was driven between the plies left to right parallel to the fibers in a predominately opening mode (Mode I). Several features of this SEM reveal a lot about fracturing in a high modulus/low toughness matrix. First, notice the very clean crack line. Very little resin has adhered to the graphite fibers adjacent to the crack with the crack transferring and running through the interface. The broken fiber is, in fact, due to fiber debond. This is suggestive of a low fracture toughness (K) value with a typical brittle failure pattern.

Second, notice that there is no deformation in the matrix right next to the fibers adjacent to the crack. This is indicative of low energy dissipation during the cracking process. Indeed, this resin has a very low critical strain energy release rate, G.

Figure 3 is a SEM of a similar epoxy resin that has been modified to increase the K and G values. Notice that particles of the matrix still adhere to the fibers and that there is extensive matrix deformation adjacent to the crack. Much of the energy propagating the crack is absorbed in deforming the matrix both ahead and out of plane from the crack front.

The SEM in figure 4 is the same as that of figure 3 except for scale. Notice that matrix deformation has occurred at least six fibers away from the crack – characteristic of energy absorption.

Matrix modulus, which is the most dominant neat resin property that translates into composite mechanical properties, is about 10 percent less up to the 140°F designed service temperature for the tough resin in figures 3 and 4. But, the K and G values are over ten times higher – an excellent tradeoff. For boat hull applications, this resin has a much better balance of properties than the less tough resin (which would be needed for higher service temperatures). This balance will most likely translate into a longer service life.

D. Two Phase Epoxy Systems

The modifications made to the epoxy resin in figures 3 and 4 change it from a single phase to a two-phase system. It is this two-phase morphology that significantly improves the excellent balance of mechanical and toughness properties. Two-phase epoxy systems have been used for a number of years in the aerospace field as adhesives because of superior peel strength. In the past five years they have been evaluated extensively as laminating resins for lightweight composite construction.

Two-phase epoxy systems differ from conventional single-phase resins in that, as they cure, a second discontinuous phase appears. What forms is a second phase microscopically and discreetly dispersed within a homogeneous first phase. The chemistry that produces this phenomena is outside of the scope of this paper but requires nothing special other than the standard mixing of the Part A and the Part B by the user. Because of the differences in refractive index, the cured system is translucent to opaque. Like any resin it is clear when first mixed.

It is this morphology that gives the two-phase epoxy system a unique balance of mechanical and toughness properties. The mechanical and overall properties derive from the homogeneous first phase while the interaction between the first and second phases produces the toughness properties. The fracture mechanism has been extensively studied. An initial crack, void or stress induced crack is formed in the homeogeneous first phase. The stressed condition causes dilation of the second phase with accompanying plastic flow or shear bend deformation of the first phase. The second phase nucleates causing a larger deformation or energy dissipation zone. Out of plane and ahead of the crack front, microcaracking as shown in figures 3 and 4 is the dominant energy absorbing and dissipation mechanism. Cavitations caused by the relaxing of the dilated second phase particles are evident in all fracture surfaces.

The two-phase epoxy systems used by the aerospace industry are pre-preg matrices that have high viscosity and require curing under conditions of heat and pressure. These same systems are unsuitable for use by boatbuilders. However, in June 1985, System Three Resins introduced a two-phase epoxy system for boatbuilding. Tradenamed, “Phase Two”, this system gels at room temperature, and then requires only a moderately low temperature cure with no pressure to achieve an excellent balance of mechanical toughness properties.

Table 1 lists both the mechanical and toughness properties for Phase Two epoxy resin. Most designers can relate to the mechanical properties; however, the actual values of the toughness properties need some basis of comparison.

The numeric values of K and G are the critical values in a Mode 1 fracture. Critical means the minimum amount of energy needed to do the job under steady state conditions, while Mode 1 is a fracture involving opening stress only.

(Most laminates fail in Mode 1 or a combination of Mode 1 and Mode 2 – shearing stresses.)

Vinyl ester, polyester and brittle epoxies have K values in the 300 to 500 range. The more flexible single-phase epoxies still suitable for boat hulls fall in the 600 to 900 range. Single-phase systems with K values higher than this generally fall below the service temperature threshold for adequate mechanicals. The very best two-phase epoxy systems qualified for aerospace use have K values in the 1500 to 2000 range. The K value for Phase Two epoxy is 2700.

The polyesters, vinyl esters, and brittle epoxies have G values starting at 200 joules/meter^2 for polyester and running through 500 j/m^2 for the brittle epoxies. The best epoxies qualified for aerospace use have G values of 1000 j/m^2 · Phase Two epoxy resin has a G value of 2600.

The principal reason the K and G values are higher for Phase Two resin than they are for the aerospace resin is that the aerospace resin is designed for good wet mechanicals at 200°F while the boat resin is designed for the same service at 140°F. Generally, toughness varies inversely to heat distortion resistance, and so the boat resin is actually tougher than the aerospace resin at room temperature.

The laminate data for Phase Two epoxy is shown in table 2. This data is comparable to the best vinyl ester resins used in boat hull construction. As we have seen, the real difference is apt to manifest itself in the degradation of mechanicals over time for the less tough vinyl ester resin.

Considering all this, why then are composite cored boat hulls not falling apart in service? The simple and most probable answer is that they are over designed. If this is the case, then a great deal of money is being wasted in both materials and labor to produce a heavier and poorer performing hull. The careful selection of a resin through consideration of both the mechanical and toughness properties along with the correct fiber match will provide the opportunity to build lighter longer lasting hulls.

With current resin technology the two-phase epoxy resin systems offer the best opportunity to reach this goal.

III Conclusions and Recommendations

Two-phase epoxy systems offer naval architects and marine engineers significant opportunities of improvement of skin laminates for composite foam and balsa cored boat hulls. These are the only resins that currently offer excellent balance between both mechanical and toughness properties.

Work with various fibers and cores using different layup schedules are needed for static and dynamic testing to maximize efficient use of materials and minimize cost.

Highly developed two phase epoxy resin systems designed for boats are now available and may be used in place of vinyl ester resins in composite core boat hulls.

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V. Acknowledgements

The SEM was provided by W.L. Bradley of Texas A&M University. The author acknowledges the guidance of R.J. Moulton of Lafayette, California in the preparation of this paper.

TABLE 1
PHASE TWO EPOXY RESIN TEST DATA

Mechanical Properties:			**Cure 1**	**Cure 2**
Tensile Strength, psi			9,600	8,800
Elongation at Break, %			7.5	3.6
Tensile Modulus, psi			470,000	460,000
Flexural Strength, psi			19,000	14,500
Flexural Modulus, psi			515,000	500,000
Compressive Strength, psi			32,000	33,000
Shore D Hardness			72	70
Glass Transition Temp., °C			72	62
Heat Distortion Temp., °C			64	50
Water Immersion Weight Gain, % (140°F, 30 days)			2.8	2.9
Toughness Properties:				
Fracture Toughness, K_{1C}, lbs.	Inch		2,700	1,600
Critical Strain Energy		j/m^2	2,600	860
Release Rate, G_{1C}		lbs/in	14.8	2.6

Rheology:

Mixing Ratio:	3 parts Resin to 1 part Converter By Weight	
	10 parts Resin to 4 parts Converter By Volume	
Density:	Resin -	9.70 pounds per gallon
(68°F)	Converter -	8.25 pounds per gallon
	Mixed -	9.29 pounds per gallon
Viscosity:	Resin -	3,600 centipoise
	Converter -	55 centipoise
	Mixed -	920 centipoise

Kinetics*

Pot Life	100 grams	105 minutes
	1 quart	75 minutes
Mold Open Time		3-4 hours
Tack Free Time		5-6 hours

* Without Accelerator
Tests conducted at 77°F, data at 77°F except as noted. Cure 1 is 7 days at 77°F, 2 hours at 140°F. Cure 2 is 7 days at 77°F.

TABLE 2
PHASE TWO EPOXY RESIN LAMINATE DATA

	CURE 1	CURE 2
Fiberglass Cloth: Clark-Schwebel 7781/CS-290 Silane Finish		
Flexural Strength at 77°F, psi	73,000	71,000
Flexural Modulus at 77°F, Msi	3.6	3.5
Flexural Strength at 140°F, psi	55,000	18,000
Flexural Modulus at 140°F, Msi	3.2	1.0
Short Beam Shear at 77°F, psi	7,600	6,700
at 140°F, psi	3,600	2,200
Fiber Volume 60%. 10 plies .105”		
Woven Graphite: Thornel or Celion. 24X24 8HS 3K or 12X12 5HS 6K		
Flexural Strength at 77°F, psi	115,000	110,000
Flexural Modulus at 77°F, Msi	9.2	9.0
Flexural Strength at 140°F, psi	80,000	25,000
Flexural Moldulus at 140°F, Msi	8.0	4.5
Short Beam Shear at 77°F, psi	8,100	6,900
at 140°F, psi	5,300	2,100
Fiber Volume 58%. 8 plies .110”		
Kevlar: 285 style, Scoured		
Flexural Strength at 77°F, psi	54,000	50,000
Flexural Modulus at 77°F, Msi	3.7	2.8
Flexural Strength at 140°F, psi	40,000	10,000
Flexural Modulus at 140°F, Msi	2.0	0.9
Short Beam Shear at 77°F, psi	4,200	3,800
at 140°F, psi	3,000	1,000
Fiber Volume 50%. 10 plies .107”		

All laminates vacuum bagged. Cure 1 is 7 days at 77°F, 2 hours at 140°F. Cure 2 is at 77°F. Msi is 1,000,000 psi