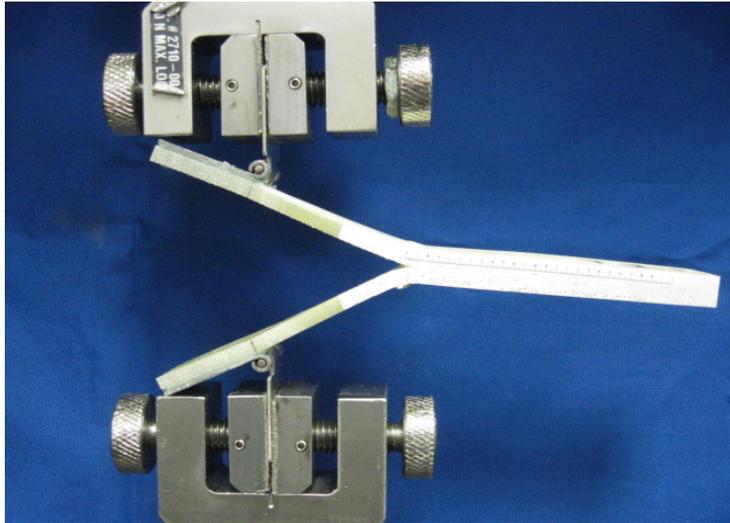


The Effect of Matrix Toughness on Composite Fracture Behavior



Derrick D. Stokes
Jackson State University
Senior, Physics & Chemistry

Applied Research Laboratory
The Pennsylvania State University
ARL Open D.O.O.R Internship Program
Summer 2009

Mentor: Composite Materials Division

August 7, 2009

Outline

Abstract.....	2
Objective.....	2
Introduction.....	2-4
Background.....	4
Experiment Plan.....	5
Fabrication of Panels.....	5-7
Fabrication of Test Specimen.....	7-8
Testing and Observations	8-9
Technical Problems	9
Experimental Results.....	9-10
Conclusions.....	10
Future works.....	10-11
Reference	12

Abstract

Polymer Matrix Composites (PMC's) are highly valued in industry as well as in the military because they have excellent structural benefits. Due to PMC's being a polymeric material, it is possible to increase the flexibility to a structure. Flexibility leads to energy absorption, which leads to a "tougher" system. The Navy has set strict regulations on PMC's, one of which being that the PCM has to have a toughness (G_{1c}) value of $4[(\text{in.} \times \text{lbs.})/\text{in}^2]$. There are few materials that consistently meet this mandate. Therefore, this regulation automatically rules out a lot of possible substitutes that may be more cost effective. Therefore, it is imperative to investigate the methods and procedures that are necessary to toughening a matrix. This is vital because a toughened matrix will correspond with a tougher composite.

Objective

Polymer matrices with efficient toughness are essential to a composite's ability to function properly. Therefore, to improve the performance of composites it is imperative that the physical properties of polymer matrices must be investigated.

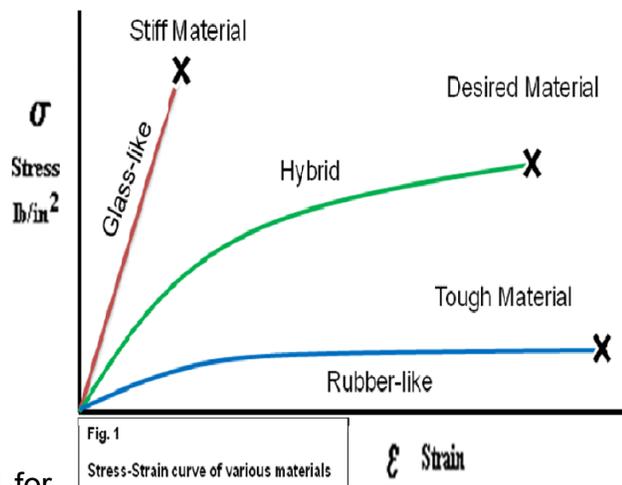
Introduction

In this experiment, our focus will be on polymer matrix composites and their structural properties. Composites are wonderful materials that have revolutionized the field of engineering. Here in, polymer matrix composites are defined as fiber-reinforced materials that are held together via some type of polymer matrix. Composites are important engineering materials because they can provide more versatility when compared to other materials such as neat polymers, ceramics, and metals. The idea behind a composite is that they are created with the purpose of combining a myriad of unique properties from different constituents to form another material.

Large funding agencies, using the Navy again as an example, are starting to look more at composites because they have excellent benefits. Benefits to using a composite may include weight reduction, cost reduction, corrosion resistance, tailoring of specific properties. A vessel that consists of composites, such as fiber and resin, will be significantly lighter in weight in comparison to a vessel that is only made of metal. Weight reduction is essential because it is, generally, the forerunner to other benefits. By constructing a lighter material one is able to travel much faster. Another benefit to a lighter vessel would be the ability to carry less fuel while still functioning properly. By

doing so, companies are able to reduce the budget by cutting fuel costs, thus, saving money. Cost reduction is vital to the survival of any company. If a company produced a product that was X dollars then that company restructured and found a way to produce a similar product for 1/2X dollars, they would be able to produce twice the amount of products using the same budget. By doing so they are able to grow and expand their company. Corrosion resistance is crucial because it prolongs the life span of a product. Even corrosion resistance is helpful in reducing a company's cost. This is evident because extending the life span equals extending the product's replacement time. Contractors care about the enhancement of structural properties of materials because they are able to go the cheaper route by using composites, while still maintaining most of the structural integrity that they would have obtained by using an all metal part. This is made possible because by combining different materials one is able to achieve the physical properties that are desired from all of the different constituents within the composite. An example of this would be creating a ceramic polymer matrix. In a ceramic polymer matrix, engineers have been able to achieve an increase in strength by using the glass fibers as structural reinforcements.

Resins are a vital factor in polymer matrix composites. Resins are highly valued for their chemical properties and are often used as adhesives. Using additives in resins have drastically improved their physical properties. Over the years, researchers have shown that there are more materials that can enhance the physical properties of resins. That particular research has led to the birth of modified resins. Modified resins are resins that have been specifically engineered for



the purpose of the advancement of their structural, physical and thermal properties. Materials such as chemicals, liquid rubber, and various rubber powders have enabled modified resins to withstand more physical punishment. We would like to manipulate a resin so that it is both very stiff and strong but at the same time be an incredibly tough system. This is very difficult because the ideal material with a high yield strength and elastic modulus would be some type of metal, such as steel; while the optimal material for toughness would be rubber (as seen in figure 1). Trying to figure out how to combine these two extremes has been an issue that has plagued the material science and engineering community for years. The Composite Materials Division at The Pennsylvania State University will help me uncover the "common ground" for what materials and methods need to be applied to a resin to enhance its toughness while

retaining its physical properties. This project is an exploratory attempt to investigate the effects of matrix toughening on composite fracture toughness.

Background

Polymer matrices are different forms of resins that are typically used in composite materials. To have a durable material or end product; it is crucial that the matrices or mediums, that hold the material together, be tough. Over the years, research has shown that it is possible to toughen a material by using different additives and techniques. As mentioned earlier; particles such as chemicals, various forms of rubber, and etc. have played a key role in toughening resins.

For instance, *Novoa et. al.* shows that rubber particles have improved the toughness of a material by increasing the impact resistance. This is achieved because the rubber particles separate out of solution and create a second phase at the material's interface. This second phase is effective in toughening because, it increases a material's fracture energy (G_{1c}) [1]. This side effect is positive because it increases a material's flexibility; which facilitates tearing instead of snapping apart, thus, extending the point of critical failure.

Although, using composites have opened many doors in the area of materials; there is still much room for growth. The Navy has a strict requirement for toughness (G_{1c}) for E-Glass epoxy systems. The Navy mandates that E-Glass epoxy systems have an Onset G_{1c} of [4.0 (in x lb/in²)]. This is a very difficult value to achieve and few materials have reached this specification. With this understanding, we must ask ourselves is such a strict specification truly necessary. This is a very pressing question because with harsh requirement, there are many materials that simply can't be used. For example, a company may have developed a wonderful material that brings down the cost drastically, operates better than the original, and is relatively much easier to produce; but this product still can't be used because it doesn't meet the G_{1c} requirements.

In this project, we will try to challenge these standards by conducting various tests using CTBN and polysulfide. These materials are good to study because they have been used as toughening agents before. CTBN stands for Carboxyl Terminated Butadiene Acrylonitrile, this typically proves more flexibility, greater adhesion, and improved fracture toughness. When curing, CTBN which is a liquid rubber, typically improves toughness much like rubber powders; the CTBN rubber particles precipitate through solution to create a second phase at the interface. Due to the fact that polysulfide is an elastomer it has similar effects, such as increased flexibility. Polysulfide is a long, elastic chain that contains sulfur atoms.

Experimentation

Experiment plan

In this experiment we investigated three different epoxy resin matrices. To do so, we tested and observed the behavior of the “neat resins” under particular conditions. The term neat resin simply means that there are no structural support systems throughout the matrix, i.e., glass fibers. It is necessary to study the matrices so it may be possible to predict how a matrix can affect a composite. The three systems tested are engineered epoxy resin blends. The three systems are described in the table below.

Polymer Matrix	Name of Matrix	Description of Matrix
1. Commercial Epoxy Resin	EPON Resin 8132 (Baseline)	Low Toughness/Brittle
2. Modified Commercial Epoxy Resin 1	EPON Resin 8132 + CTBN	Intermediate Toughness
3. Modified Commercial Epoxy Resin 2	EPON Resin 8132 + Polysulfide	Enhanced Toughness

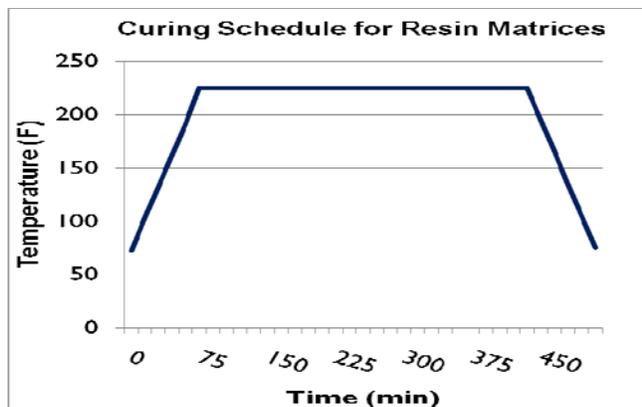
The first resin is EPON 8132; this is our control or baseline resin. The second resin is EPON 8132 with CTBN as an additive. CTBN was chosen because it is a liquid rubber and it is a material that is commonly used in toughening experiments. The CTBN typically provides greater adhesion and improved fracture toughness. The reason this happens is because the rubber particles in the CTBN will precipitate through the solution and create a second phase at the interface. In this second phase the rubber particles are dilated to about the size of ten microns (10 μ). This action is one way to increase the fracture energy, G_{1c} , of a material. The third material is EPON 8132 with Polysulfide as an additive. Although this material hasn't been used too often in toughening experiments it has properties that, if used properly, can be very beneficial to composites. Polysulfide is an elastomer, meaning that it is a polymer with elastic properties. Due to this fact, polysulfide is able to deform and stretch materials and make them more flexible. As mentioned earlier, the proper amount of flexibility is necessary for toughening a material.

Fabrication of Resin Panels

In processing the matrix for the panels we employed a “pre-react” method for material 2 and material 3 [(8132+CTBN) and (8132+Polysulfide)]; meaning that we

physically reacted additives with the epoxy to form what is known as an adduct. We used chemicals such as DMP30 and PACM20 as catalysts for the matrix. Once the proper components were added to the matrix we had to thoroughly blend the mixture by using an electric drill. After blending, it was essential to then degas the matrix. Degassing is vital to the structural integrity of the matrix because it reduces the amount of voids (gaps) once the resin cures. Once thoroughly degassed, the matrix is placed in an oven where it can go through a curing cycle.

We used a specific curing schedule because temperature and time had to be considered. The chosen schedule was set for the oven to go from room temperature (72 °F ± 4 °F) to 225 °F in 75 minutes which was 2°F per minute. Once at 225 °F the oven held that temperature constant for 360 minutes (6 hours). The temperature in the oven then cooled back down to room temperature (72 °F ± 4 °F) in 60 minutes as shown in the figure above.



Material 1 is the control or baseline for the experiment. The components for material 1 are EPON Resin 8132 and Bis (p-aminocyclohexyl) methane. The common name for Bis (p-aminocyclohexyl) methane is PACM20 which is an amine curative. The target formula used is 100 parts EPON Resin 8132 by 25.4 parts PACM20. Our target weight for the EPON Resin 8132 was 846g; if that that is 100 % then 215g of the PACM 20 would be needed to reach 25.4%.

Material 1

Components	Target %	Target (g)	Actual %	Actual (g)
EPON Resin 8132	100%	846g	100%	846g
PACM 20	25.4%	215g	100%	215g

Material 2 is the modified epoxy resin that is based upon 8132. The components for material 1 are EPON Resin 8132, CTBN (liquid rubber), and PACM20. The target formula is 100 parts EPON Resin 8132 by 20 parts CTBN. The target weight for the

EPON Resin 8132 is 890g; if that that is 100% then 179g of the CTBN would be needed to reach 20%. These components are then blended to create the modified mixture. The formula for the modified mixture is 100 parts modified mixture 1 (EPON Resin 8132 + CTBN) by 23.5 parts PACM20. The modified mixture is 1069; therefore, 251g of the PACM20 would be needed to reach 23.5%.

Material 2

Components	Target %	Target (g)	Actual %	Actual (g)
8132	100%	890g	100%	710g
CTBN	20%	179g	20%	140g
Modified Mix 1 (8132+CTBN)	100%	1069g	100%	850g
PACM 20	23.5%	251g	23.5%	200g

Material 3 is also a modified epoxy resin that is based upon 8132. The components for material 1 are EPON Resin 8132, Polysulfide, and PACM20. The target formula is 100 parts EPON Resin 8132 by 10 parts Polysulfide. The target weight for the EPON Resin 8132 is 680; that being 100%, 68g of Polysulfide is needed. Once the components were blended, PACM20 was added to the mixture. The formula for the total mixture is 100 parts modified mixture 2 (EPON Resin 8132 + Polysulfide) by 14.6 parts PACM20. The modified mixture is 748g; therefore, 109.5g of the PACM20 was used so that the target goal of 14.6% was reached.

Material 3

Components	Target %	Target (g)	Actual %	Actual (g)
8132	100%	680g	100%	721
Polysulfide	10%	68g	20%	72.1g
Modified Mix 2 (8132+CTBN)	100%	748g	100%	793.1g
PACM 20	14.6%	109.5g	23.5%	116.1g

Fabrication of Test Specimens

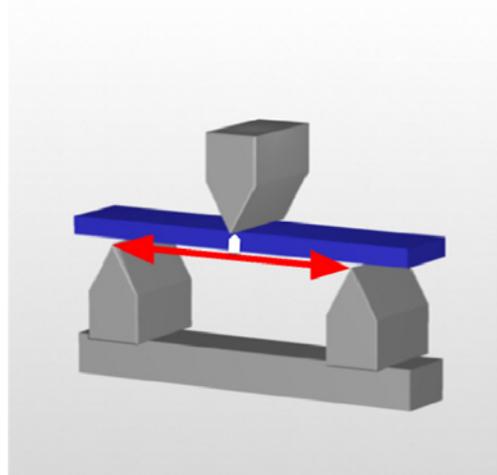
In testing the toughness of the specimen, Single Edge Notched Bend (SENB) and Tensile tests were employed. The SENB test was a good way of measuring the

toughness of the matrix because it is a test that uses a three point bend with the load focused above the notch. The Tensile test provides other important structural information such as: Tensile Yield Strength, Tensile Modulus (stiffness), and Poisson's Ratio.

Testing and Observations

Matrix Specimen

The SENB (shown in the figure to the rt.) test an essential test for defining toughness in a matrix. This test provides a Mode 1 separation. From this test and principles based off linear fracture mechanics, it is possible to take the data and find the P_Q . P_Q is the point at where the matrix starts to deform plastically (won't return to original shape). Once P_Q is found its deflection is used as the upper limit of integration, this is necessary to find the energy under the curve (U) on a Load vs. Deflection graph. To find the toughness from this energy, a series of equations must be used. The equation that is



uses to energy and converts it into a toughness (G_{1c}) value is $G_Q=U/ (BW\Phi)$ [2].

U= Energy

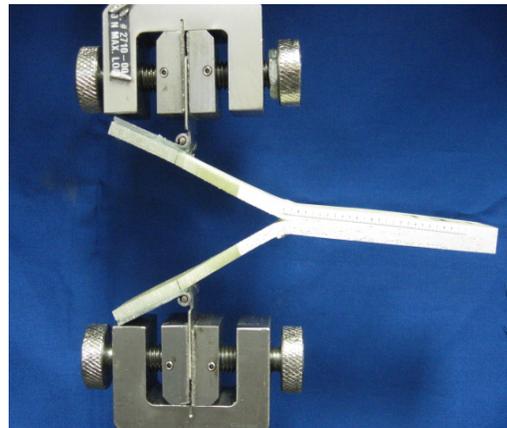
B=Thickness of specimen

W=Width of specimen

$\Phi= [(A+18.64)/ (dA/dx)]$

Composite Specimen

In fabricating the test specimen; E glass 3783 was used as structural support for the matrices. Each specimen was composed of 16 plies of E glass 3783 that were aligned in the zero or warp direction (shown in the figure to the RT.). The same resin formulation and procedures were used on the composite panels. The E glass plies were then infused with the polymer matrix via a technique called Vacuum Assisted Resin Transfer Molding (VARTM). VARTM uses a vacuum to push



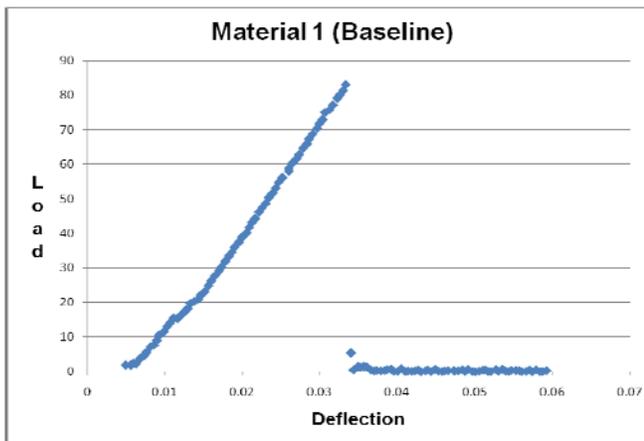
the resin from an external reservoir throughout the E glass plies. VARTM is a good bonding method because it enables resin to be infused throughout a part without leaving much air inside. That is a major benefit because air molecules can cause voids in a product and may negatively affect the materials toughness. Once the part has finished running through the aforementioned curing schedule, it was then machined into Double Cantilever Beam (DCB's). DCB's are used for Mode1 (delaminar) testing where they measure the load and deflection of a specimen to determine the toughness (G_{1c}) of a composite; whereas SENB's are used for polymeric matrices.

Technical Problems

There were a few technical issues that occurred in the project, one being the second phase of the CTBN. The rubber molecules in the CTBN failed to dilate to about 10 microns. After the matrix for Material 2 cured, it was evident that the rubber particles successfully precipitated and created a second phase but the molecule size were on the nanoscale instead of the necessary 10 microns. Due to this issue, coupled with lack of materials and time constraints, it was not possible to test this material in a composite. Material 3 was extremely difficult to degas and was able to be infused in the E Glass 3783 via VARTM. Due to this difficulty, Material 3 had to be infused via "wet lay-up". Meaning that the resin had to be applied ply by ply, this made it possible for voids to be inside the composite.

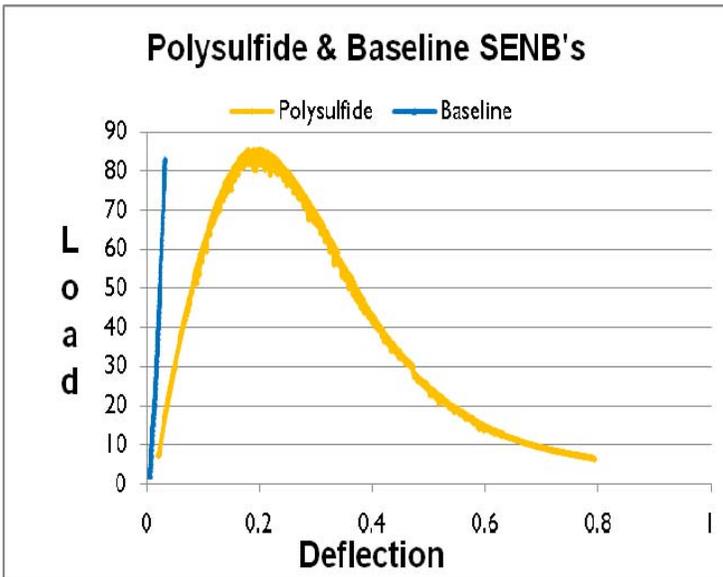
Results

Overall the results of the project were positive, despite technical issues, and outperformed the ASTM specifications. In Material 1, which was our baseline, we had a good fracture toughness of 16.8797 (in $\times \text{lb}/\text{in}^2$) but the Onset toughness was 1.762. This material also had a Post Crack Toughness of 0.0 because once P_Q was reached the material failed in a catastrophic fashion. This Onset toughness is disappointing because, as mentioned earlier, the Navy requires an Onset G_{1c} of [4.0 (in $\times \text{lb}/\text{in}^2$)].



Another disappointment was that the final composite toughness for Material 2 couldn't be determined. This was due to the fact that the rubber molecules in the CTBNs second phase were not large enough to have an affect on the toughness. The

positive aspect of the project was Material 3 because it was so tough that it outperformed the ASTM standards. The ASTM standard states that only the data up to P_Q is valid. This is true because then it is possible to compare one material to another. One fact that must be considered is the Post Crack Toughness of a material. For instance, in Material 1 the specimen snapped once P_Q was reached; while Material 3 continued to become strong until maximum strength is achieved. Material 3 still doesn't exhibit such a catastrophic failure even after maximum strength is reached. Material 3 fails in a



tearing fashion instead of snapping like Material 1 (shown in figure to the RT.). Due to the regulations of the ASTM standard (D 5045) we are unable to compare the overall toughness of Material 3 to the other two. Although, Material 3 has a low fracture toughness of 9.3462 (in x lb/in²) it is still the toughest overall material because it had a Post Crack Toughness of 247.84 (in x lb/in²). Due to the material being so tough, it didn't fail in the Double Cantilever Beam (DCB) test. The material deformed in such a fashion that its specimen remained intact but the specimen experienced compression damage to the exterior of the composite.

Conclusions

From this project it can be said that toughening a matrix will increase the toughness of a composite. Another thing that has been determined from this project was that the toughness of a matrix does not directly translate to the toughness of a composite. This is evident because, according to ASTM D5045, Material 3 had a low G_{1c} . Meaning that a matrix that has a toughness of 9.3462 (in x lb/in²) should not be able to produce a composite that will not fail or has an infinity, ∞ , toughness value.

Future works

This project has untapped potential and may eventually be a major factor in Polymer Matrix Composites (PMCs) in the future. Before this happens there are some issues that must be addressed, such as the CTBN rubber particles. There needs to be an optimal processing parameters established for the enhancement of the CTBN.

Another issue that could be addressed is the Polysulfide formulations. Due to the quick reactivity and high viscosity of Polysulfide it hard to VARTM, therefore, better formulations of Polysulfide could produce a better composite.

References

- 1.) Novao PJRO (Novoa, Paulo J. R. O.), Ferreira AJM (Ferreira, Antonio J, M.), Marques AT (Marques, Antonio Torres) (2006). Mechanical Performance of Unsaturated Polyester Resins Modified with Power from Scrap Tyre Rubber. Advanced Materials Forum III, Pts 1 and 2, 514-516, pgs. 662-665.
- 2.) March 2007. Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release of Plastic Materials. ASTM International Standard D5045.