The Effect of Processing, Glass Finish, and Rheology on the Interlaminar Shear Strength of a Woven e-Glass Reinforced Polymer Matrix Composite

George B. Piotrowski, Marty Choate, and Scott Lucas
Isola

Abstract
Laminated woven glass reinforced polymer matrix composites (PMC) are commonly used in the electronics industry as a robust and effective substrate for circuit boards. In such applications, reliability is extremely important. The laminated composites must undergo several processing steps to introduce circuitry, during which interlaminar damage is sometimes introduced, leading to blisters and delaminations. Therefore, it becomes important to understand the factors that control the interlaminar shear strength (ILSS) of the laminate. In this study, the ILSS of a laminated PMC was examined as functions of matrix phase additions, the matrix mixing procedure, the glass fiber finish chemistry and concentration, and the matrix rheology. Matrix phase additions, mixing, and glass finish were found to significantly effect the ILSS, while the matrix rheology had less of an impact.

Introduction
Multilayer printed circuit boards (PCBs), like other laminated polymer matrix composites (PMCs), are subject to ply delaminations. Delamination can be due to several factors; the most common of which are poor construction and poor processing [1-5]. Once a delamination occurs, the PCB must be scrapped. The associated increase in scrap material associated with manufacturing will generally increase the final cost of the material to account for the losses in both material and processing time. Therefore, it becomes imperative to find the causes of ply delamination and work to reduce and eliminate them.

Typical ply delaminations in PCBs occur at or near edges and surfaces of the laminate [1, 2, 4]. This is due, in large part, to two factors. The first is that laminated composites are typically characterized as being infinite planes, modeled in plane stress. In reality, there is a transition from the typical plane stress behavior to plane strain at the laminate edges. This allows for a stress in the z-direction [1, 2]. Since the bond in the z-direction is somewhat weaker than in the x and y laminate directions, owing to a lack of reinforcement, the z-axis stress induces ply delamination, starting at the free surfaces and edges. The weaknesses along z-axis are exacerbated by differences in the coefficients of thermal expansion (CTE's) between components in the laminated composite, where the CTE of the polymer matrix is significantly greater than that of the relatively low CTE of the woven e-glass fabric. To overcome the CTE differences, filler materials are added to provide some reinforcement off of the principle x-y axis. The second common cause of ply delamination is much more straightforward. During processing, corners and edges may become damaged. The damage can propagate along ply interfaces, leading to failure of the laminate. Based on these observations, it becomes apparent that three ways to reduce the number of ply failures in the z-direction are to increase the resin-to-resin bond strength, to increase the strength of resin-to-glass interface, and to minimize differences in the thermal properties of the laminate components.

In this study, the delamination behavior of a laminated e-glass reinforced polymer matrix composite was examined versus changes in the processing of the polymer matrix; and versus changes in the resin matrix rheology and in the e-glass finish chemistry and concentration.

Experimental Procedure
The material under study is a 0^{o}-90^{o} woven e-glass reinforced resin matrix composite. The PMC was processed at Isola Laminate Systems' Chandler facility following the procedures outlined by Isola (Isola Group, Chandler, AZ). For the experiment, processing factors under study included the resin mixing procedure, resin filler additions, and the base resin viscosity. Experiments examining changes in the resin matrix were performed over the course of two DOE trials. The first being a two factorial experiment examining high and low matrix particle filler content and the method of dispersion by a) Ross mixer type and b) Cowles mixer type Table 1. The second as a larger three factorial experiment examining resin viscosity via changes in the molecular weight of the resin and changes in the e-glass sizing, Table 2. The results obtained from the first DOE trial were used to select the samples used for the second DOE trial. The effects of changes in ply construction are well established by others [1-4] and will not be covered here. For the two DOE trials, the glass fiber diameter and the bulk matrix resin contents were kept constant. All efforts were made to produce symmetric, unidirectional laminates.

Table 1, 2^2 Factorial Design of Experiment Study.

2^2 Factorial Design		+	High Filler	Ross	
		-	Low Filler	Cowles	
	Test	**Run Order**	**Filler**	**Mixing**	**Filler x Mixing**
	1		+	+	-
	2		-	+	+
	3		+	-	-
	4		-	-	+

Table 2, 2^3 Factorial Design of Experiment Study.

2^3 Factorial Design in 2 Blocks	+	Low MW	Silane 1	Silane 3	Low Visc				
	-	High MW	Silane 2	Silane 4	High Visc	RVxB	STxSC	SCxB	
	Test	**Run Order**	**Resin Visc (RV)**	**Sizing Type (ST)**	**Sizing Conc (SC)**	**Blocked Factors (B)**	**STxSC**	**RVxSC**	**RVxST**
	1		-	-	+	+	-	-	+
Block 1	2		+	-	-	+	+	-	-
Low Visc	3		-	+	-	+	-	+	-
Low MW	4		+	+	+	+	+	+	+
	5		+	+	-	-	-	-	+
Block 2	6		-	+	+	-	+	-	-
High Visc	7		+	-	+	-	-	+	-
High MW	8		-	-	-	-	+	+	+

The factors under study were chosen in an attempt to produce quantifiable differences in the interlaminar shear strength (ILSS) of the PMC. The ILSS was measured using an electric drive load frame, following the procedure outlined in ASTM #D2344 [6]. Since the test method can yield fracture behavior inconsistent with the ILSS, care was taken to ensure that the fracture mode was indeed shear and not tensile, compressive, or inelastic deformation, Figure 1.

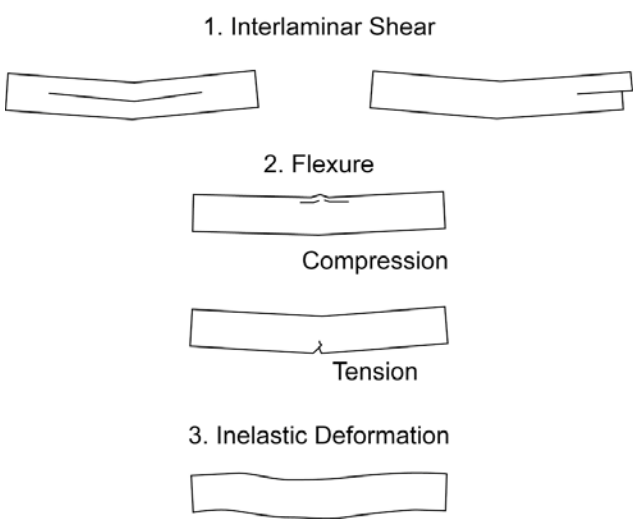

Figure 1. Modes of Short-Beam Failure

For the first DOE, samples were examined with higher amounts of particle filler in the matrix phase, greater than 20%, and with lower amounts of filler, less than 7%. Changes in dispersion were examined for the high and low particle filler content levels using a high dispersion Ross mixer (Model: ME100LX, Charles Ross & Son Company, Hauppauge, NY) and using a low dispersion Cowles mixer (Model: CM-100, Morehouse-Cowles Inc., Fullerton, CA).

Examination of the glass fiber sizing properties was carried out as part of the three factorial DOE, with changes in the resin viscosity, and the woven e-glass reinforcement. The resin viscosity was examined with high and low flow, based on changes in the molecular weight of the base resin. Examination of the glass reinforcement involved alterations of the silane sizing applied to the e-glass, where the silane chemistry and the silane concentration were studied. For the two DOE trials, the glass fiber diameter and the bulk matrix phase fractions were kept constant.

Results and Discussion

Effect of Filler Content and Mixing

The effect of various mixing processes in particle reinforced composites cannot be understated. Typically, as a particle-reinforced system becomes more homogeneous, the detrimental effects of phenomena such as particle clustering are reduced. This leads directly to increases in the mechanical strength of the material due to a decrease in the number of stress concentrators present in the microstructure [7,8]. It follows that changes in the particle filler content and the dispersion method may cause variations in the ILSS.

The two factorial DOE examined relative high and low particle filler contents with changes in the dispersion method in an attempt to optimize the ILSS. Beginning with the changes in the filler content, it was found that a reduction from the higher content to the lower filler content led to approximately a 12% increase in the ILSS in the highly dispersed Ross-mixed system, but no significant increases in the conventionally mixed Cowles system, Table 3. The increase in ILSS that was observed for the Ross mixed system suggests that the dispersion method is more a factor than the actual filler content.

Indeed, comparison of like systems with changes in the dispersion method indicates that the higher the degree particle exfoliation, the greater the ILSS. Regardless of the filler content, samples that were homogenized with the high dispersion Ross mixer exhibited a higher ILSS value than those processed with a Cowles mixer, Table 3. An increase of approximately 5% was observed for the higher filler content samples, while an increase of approximately 18% was observed for the lower filler content samples. Removal of the particle filler acted to further increase the ILSS, suggesting that while the addition of particle fillers in the e-glass reinforced system are beneficial to the thermal properties of the composite, they are detrimental to the interlaminar bond.

Table 3, Effect of Filler Content on the ILSS with Like Mixing.

Sample	ILSS (psi)	Percent Change from High Filler Content, Like Mixing (%)	Percent Change from Cowles Mixing, Like Filler Contents (%)
Cowles Mixed, 20% Filler	2703.5 +/- 66.1	-	-
Ross Mixed, 20% Filler	2842.5 +/- 114.3	-	~ 5.15
Cowles Mixed, 7% Filler	2695.9 +/- 161.4	~ - 0.28	-
Ross Mixed, 7% Filler	3188.0 +/- 121.1	~ 12.15	~ 18.25

In general, filler materials are added to PMC's to offset the differences in CTE between the composite components. Laminated PMC's are highly reinforced along the x- and y-axes, owing to the woven glass phase. This is partly due to the low CTE of the glass, and partly due its higher modulus. As a result, damage tends to occur in directions off of these reinforced axes, typically along the unreinforced z-axis. When particle fillers are added to the laminate, there is some reinforcement of the z-axis owing mostly to a decrease in the z-axis CTE. The drawbacks of using particle filler materials are many. If too much filler material is added to the system, there tends to be particle clustering, creating areas of high stress intensity [7-9]. Likewise, if the bonding between the particle filler and the matrix phase is not optimized for chemical and mechanical compatibility, the filler may have a weakening effect on the composite [1]. What the study in question answers is the degree to which particle fillers weaken the ILSS of the laminate, and to what effect particle exfoliation has on the shear strength.

The increases the shear strength noted from the introduction of a high dispersion mixing procedure and from the reduction in the filler content help to solidify the notion that homogenization of the composite microstructure is beneficial to the mechanical properties of the laminate. Comparison of the microstructure for the four systems provides some insight into this phenomena, where the highly filled and Cowles mixed system shows evidence of large filler clusters agglomerating at weave crossover points in the e-glass fabric used as the reinforcement phase, Figure 2a. The "particle drifts" observed at the weave crossovers likely act as sites of poor interlaminar bonding, creating regions prone to delamination. In contrast, the Ross mixed systems, specifically those with relatively lower filler content, lack these "particle drifts" in large quantities, and while still present, are greatly reduced in size, Figure 2b. This leads to the increased shear strength values observed. Note that in both cases, as in the majority of the specimens examined in this work, the failure mode is resin-to-glass.

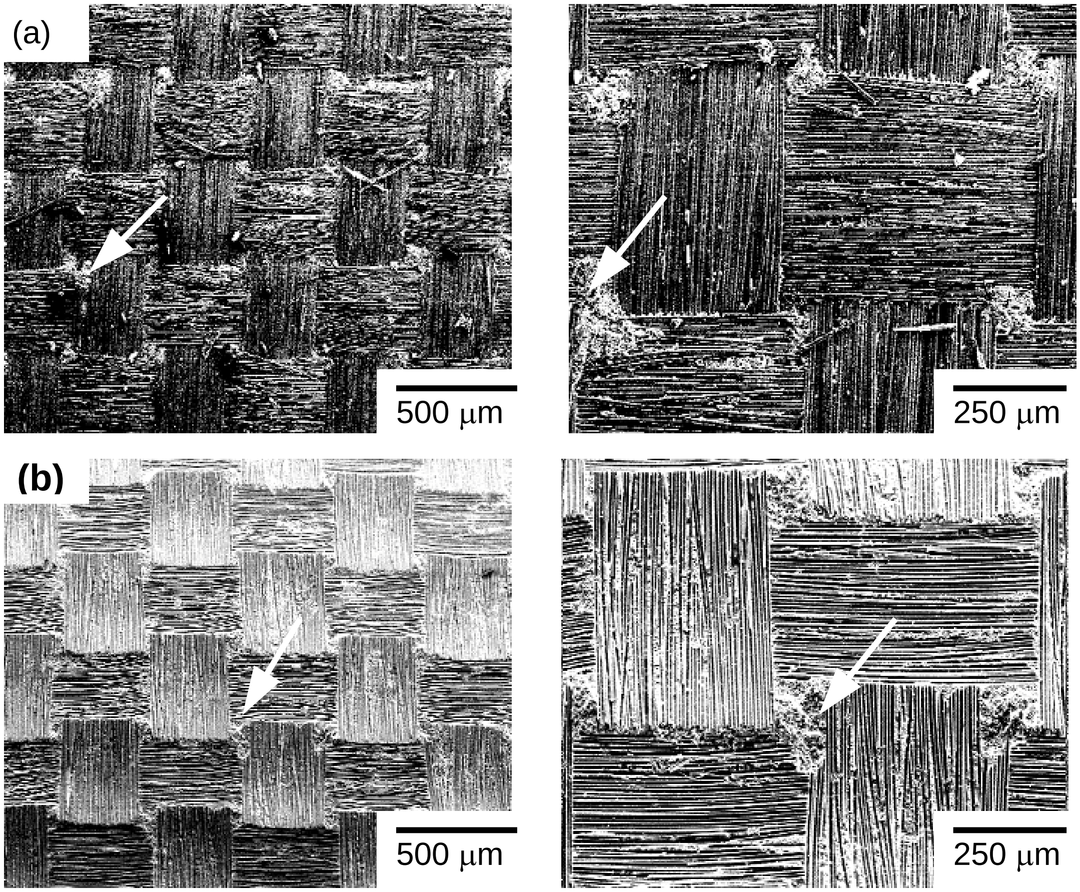

Figure 2, Filler Content and Matrix Mixing Effects on Particle Agglomeration (a): Highly filled, Cowles mixed (b): Low filler, Ross Mixed.

Effect of Resin Rheology and e-Glass Sizing

The second part of the study examined the effects that the resin rheology and the e-Glass sizing had on the ILSS. Examination was carried out as a DOE trial, with the resin rheology, the e-Glass sizing chemistry, and the e-Glass sizing concentration acting as the factors under study. Using the results of the first DOE, only samples from the Ross mixed system with lower filler content were included as test specimens.

Two different rheologies were examined, a relative high and a relative low. The resin rheology was examined by altering the molecular weight of the base resin while maintaining the same polymer backbone. In this way, the bulk electrical and physical properties of the laminate were maintained, while the fiber wetting characteristics of the resin were altered. It follows that the lower molecular weight resin will have better fiber wetting characteristics, owing to the lower viscosity and lower surface tension. The increase in fiber wet-out should then, in turn, increase the ILSS.

Examination of the results of the rheology experiment suggests that the percent flow of the resin does not affect the ILSS of the laminate at the flow levels examined, Figure 3. Thus over the flow ranges typically incurred during standard processing flow is not a significant factor in determining the ILSS of the laminate.

Since no significant changes were observed between the high and low flow samples, the experiment was extended to include a sample with a viscosity approximately two and a half times (2.5x) higher than the relative high flow samples. The results of the extended examination suggest that flow does have an impact on the ILSS, with the large increase in flow actually decreasing the ILSS, contrary to what was hypothesized, Figure 3. The decrease in ILSS may be due to the formation of internal voids resulting from processing at higher flow matrix flow values, where improper wetting of the glass fabric may occur, or the resin matrix may be under-cured.

When performing a DOE experiment, it is always important to choose the correct levels for all the experimental controls. In the case of the second DOE trial, the initial levels of the experimental controls were chosen more closely mimic the average

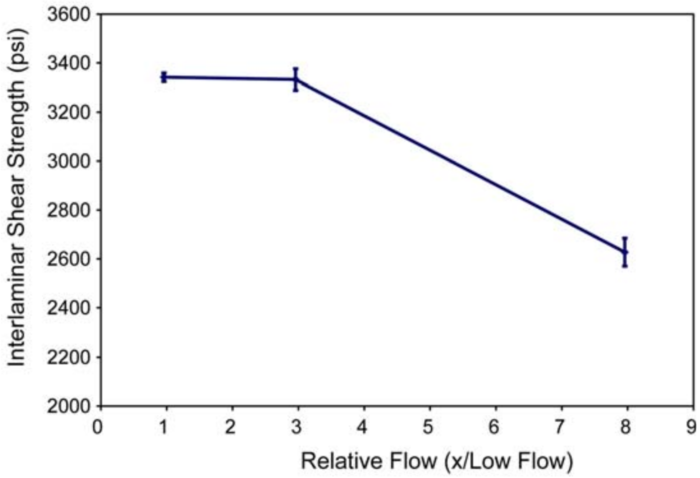

Figure 3, ILSS vs. Resin Rheology.

Silane	Chemistry	Concentration
A	1	1x Silane A
B	1	2x Silane A
C	2	1x Silane C
D	2	3x Silane C

Table 4, Silane Types and Concentrations Examined.

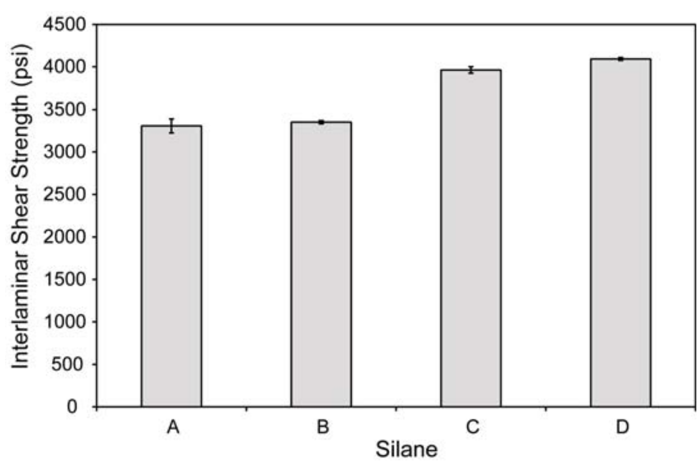

Figure 4, Effect of Silane Chemistry and Content on ILSS.

processing conditions. As was evidenced, for the processing levels chosen, the changes in the resin matrix rheology had little to no impact on the shear strength, whereas a dramatic increase in the flow resulted in a significant decrease in the shear strength. Based on the results, it is now known that there is a limit to which the flow of the resin can be increased before the increases become detrimental. The results of this experiment underscore the importance of careful examination of problems prior to action and experimentation to insure that the results are valid for as wide a range of conditions as possible.

Following examination of the resin rheology the effect of the e-glass fiber sizing was examined. Four different sizings were examined, with two concentrations each from two different types of silane, Table 4. Since the two sizing agents are different, the concentrations present had a different affect on each. However in general, increases in the sizing concentration tend to asymptotically increase the ILSS, [10, 11]. For the experiment, the silane chemistry was seen to be the dominant factor, with only cursory increases in the ILSS seen with changes in the silane concentration, Figure 4. The changes associated with altering the e-Glass finish can be explained in terms of the compatibility of the silane chemistry with the resin matrix chemistry.

It follows that determining the correct functional group on the silane compound has a very significant impact on the ILSS of the composite. Following the reversible bond theory proposed by Plueddemann [12], the weak links in the glass-silane-polymer bond are the functional groups attached to the organosilane. At higher shear strains, the weaker silane-polymer bonds will fail prematurely, leading to delamination at the resin/glass interface. Optimization of the silane chemistry and concentration with the matrix chemistry led to an increase in the ILSS of nearly 25% from the lowest observed value.

Conclusions

The engineering and economic problems associated with ply delaminations in laminated composites are numerous. As a result it is imperative to find and reduce the root causes of poor interlaminar shear strength. In this study, five factors were examined in an attempt to see how they affect the shear strength of a laminated e-Glass reinforced polymer matrix composite. Based on the study, the following statements can be made:

- The addition of particle filler materials, while beneficial in minimizing thermal property mismatches, appear to be detrimental to the ILSS of the laminate, due to the tendency of the particles to agglomerate at fiber crossover points.

- High dispersion mixing of the system to homogenize the composite microstructure can reduce the size and frequency of such agglomerates at the weave crossover points, thereby increasing the ILSS of the composite.

- The resin rheology does not appear to affect the ILSS for flow values in the normal operating range, in typical processing, however, at higher flow values than are typically encountered during standard processing the ILSS decreases significantly.

- The silane sizing employed on the woven e-Glass fibers must be tailored for chemistry and concentration with the chemistry of the matrix phase to optimize the shear strength of the laminate.

References

1. K.K. Chawla, *Composite Materials: Science and Engineering, Second Edition*, 1998, Springer, New York.
2. N.J. Pagano and R.B. Pipes, “Interlaminar Stress in Composite Laminates Under Uniform Axial Extension”, 1971, 4, J. Composite Mater., 538-548.
3. E.A. Phillips, C.T. Herakovich, and L.L. Graham, “Damage Development in Composites with Large Stress Gradients”, 2001, 61, Composites Sci. & Tech., 2169-2182.
4. L.J. Hart-Smith, “A Re-Examination of the Analysis of In-Plane Matrix Failures in Fibrous Composite Laminates”, 1996, 56, Composites. Sci. & Tech., 107-121.
5. L. Gautier, B. Mortaigne, and V. Bellenger, “Interface Damage Study of Hydrothermally Aged Glass-Fibre-Reinforced Polyester Composites”, 1999, 59, Composites Sci. & Tech., 2329-2337.
6. “ASTM D 2344/D 2344M-00e1 Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates”, 2005, 15.03, ASTM International, West Conshohacken, PA.
7. L. Ye and K. Friedrich, “Mode I Interlaminar Fracture of Co-Mingled Yarn Based Glass/Polypropylene Composites”, 1993, 46, Composites Sci. & Tech., 18-198.
8. C.K. Lam, H.Y. Cheung, K.T. Lau, L.M. Zhou, M.W. Ho, and D. Hui, “Cluster Size Effect in Hardness of Nanoclay/Epoxy Composites”, 2004, Composites Part B: Eng., *Article In Press*.
9. Y.-L. Shen, J.J. Williams, G. Piotrowski, N. Chawla, and Y.L. Guo, “Correlation between Tensile and Indentation Behavior of Particle-Reinforced Metal Matrix Composites: an Experimental and Numerical Study,” *Acta Mater*., 2001, 49, 3219-3229.
10. R. H. Podgaiz and R.J.J. Williams, “Effects of Fiber Coatings of Mechanical Properties of Unidirectional Glass-Reinforced Composites”, 1997, 57, Composite Sci. & Tech., 1071-1076.
11. N.A. St. John and J.R. Brown, “Flexural and Interlaminar Shear Properties of Glass-Reinforced Phenolic Composites”, 1998, 29A, Composites Part A, 939-946.
12. E.P. Plueddmann, *Silane Coupling Agents*, *Second Edition*, 1991, Plenum Press, New York.