Effect of Toughening and E-Glass Sizing on Fracture Toughness and Delamination in High Thermal Stability Electrical Laminates

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1.0 Introduction

Mechanical drilling of through-holes is an important process for the manufacture of printed circuit boards (PCBs). The quality of a through-hole is measured by its ability to interface with the plating, soldering, and formation of a highly reliable, non-degrading electrical and mechanical connection. To address the mechanical integrity of a board subsequent to these processes, new chemistries that can sustain high process temperatures are being applied for manufacture of electrical laminates. These chemistries are deliberately designed to increase the glass transition and thermal decomposition temperatures (T_g and T_d) of the resin particularly to sustain high melting temperature lead-free solder reflow processes. However, such materials are unable to sustain high mechanical stresses during the board drilling process for through-hole fabrication due to brittleness.

Drilling of brittle laminates can result in cracking, delamination, and drill-bit wear and breakage. Although the drilling equipment, drill bits, and drilling parameters can be optimized to minimize these problems, additional efforts are desirable to improve the drillability of the PCBs. Because the drilling process is a very expensive step in the device fabrication process, drilling parameters are optimized to obtain high quality drill-holes and to minimize drill bit wear. The challenge arises from the fact that engineering process changes have not been successful in reducing drilling defects without significantly influencing the economics. Therefore, additives that improve the toughness of the resin are typically employed as they are more cost effective than process engineering solutions.

In this work we report results of the fracture toughness of a high thermal stability resin system toughened by The Dow Chemical Company proprietary particulate-type toughening material. Results show a significant improvement in the fracture toughness with minimum impact on other thermomechanical properties such as T_g and T_d. Because delamination in electrical laminates is a critical failure mechanism observed in such systems, we also investigated the potential synergistic impact of the toughening material (FORTEGRA™ 351) and glass sizing on adhesive properties of the laminate board. Results showed improvements in both shear and tensile strengths of the test vehicles with the addition of the toughener for two different glass finishes. A drilling test showed significant delamination failure for a non-toughened board as observed by a large halo around the drill-hole, and a punch test yielded similar results. Further, it was shown that copper peel strength improved with the addition of the toughener for the two different glass finish types studied. These results are important because they show that use of the toughener and appropriate choice of glass-finish will significantly improve the thermomechanical integrity of high thermal stability test vehicles during downstream part fabrication processes.

The integrity of the fiber-matrix interface plays a very critical role in the performance of the electrical laminate subsequent to thermal stresses as experienced in reflow processes or mechanical stresses as those that the laminate is subjected to during the drilling process. Various chemistries are applied to fiber surfaces, creating a "finish" that creates the interface that improves the interaction between glass and resin. The interaction between glass and resin is very important in the downstream performance of electronic parts because delamination in the glass-matrix interface is the main failure mode[1,2]. Therefore, glass manufacturers spend a substantial amount of resources to develop glass-finish chemistries that are specific to resin systems. In this work, we compare the effect of two proprietary glass-finish chemistries made by JPS Composites on a high thermal stability resin system. Additionally, we studied the impact of the toughener technology on the resin system in terms of fracture toughness and key laminate thermomechanical properties.

2.0 Experimental

2.1 Materials

A model high thermal stability epoxy resin formulation based on phenol-novolac chemistry was used in these studies. Laminate boards were prepared from 8 B-staged prepregs prepared on 7628 glass.

The prepreg resin content was maintained at ~ 45 wt%. Boards were prepared from a non-toughened formulation and a formulation toughened with the particulate toughening material.

2.2 Sample Preparation

The formulation of interest was prepared by blending the components in methyl ethyl ketone (MEK) and shaking until homogeneous. The solution-based toughener was then added to the formulation and paddle-mixed for a few minutes. The solids content of the final formulation was adjusted to obtain a viscosity of "B" using Gardner bubble viscosity standards.

The reactivity of the varnish was measured using the Stroke cure test. A few grams of sample were placed on a hot plate at 171 °C and stroked using a wooden spatula. The elapsed time in seconds required for gelation, as indicated by a sudden increase in the viscosity, is the resin reactivity with a target of 260 seconds. Additional catalyst was added as needed to adjust the reactivity.

2.3 Fracture Toughness

Fracture toughness measurements were performed on bulk neat resin samples using the compact tension (CT) geometry. ASTM 5045 was used to obtain the critical stress intensity factor K_{1C} since all specimens adhered to linear elastic fracture mechanics characterized by a linear load-displacement curve during initial loading of the sample followed by a catastrophic crack propagation event. Samples were pre-notched by using a razor blade prior to testing.

2.4 Copper Peel Strength

Copper peel was measured using an IMASS SP-2000 slip/peel tester equipped with a variable angle peel fixture capable of maintaining the desired 90° peel angle throughout the test. For the copper etching, 2"x4" copper clad laminates were cut. Two strips of ¼" graphite tape were placed lengthwise along the sample on both faces of the laminate with at least a ½" space between them. The laminate pieces were then placed in a KeyPro bench top etcher. Once the samples were removed from the etcher and properly dried, the graphite tape was removed to reveal the copper strips. A razor blade was used to pull up ½ of each copper strip. The laminate was then loaded onto the IMASS tester. The copper strip was clamped and the copper peel test was conducted at a 90° angle with a pull rate of 2.8 in/min.

2.5 Moisture Uptake and Solder Dip

The moisture uptake was determined by putting pre-weighed 2" x 3" coupons of laminates in an autoclave at 122 °C for 2 h. The coupons were then removed from the autoclave, cleaned and re-weighed. The weight difference between the pre-autoclave and post-autoclave samples scaled by the initial weight of the coupons was determined as the percentage moisture uptake. The conditioned samples were then dipped into the 288 °C solder for 20 seconds and visually inspected for blistering and delamination.

2.6 Flex Strength

Most commonly the specimen lies on a support span and the load is applied to the center by the loading nose producing three-point bending at a specified rate. The parameters for this test are the support span, the speed of the loading, and the maximum deflection for the test. These parameters are based on the test specimen thickness and are defined differently by ASTM and ISO. For ASTM D790, the test is stopped when the specimen reaches 5% deflection or the specimen breaks before 5%. For ISO 178, the test is stopped when the specimen breaks. If the specimen does not break, the test is continued as far as possible and the stress at 3.5% (conventional deflection) is reported.

2.7 Short Beam Shear Strength

The test is described in ASTM D 5379. A specimen notched on both sides is clamped in a special device which is held longitudinally. When compressed, this creates a zone of torque-free shear load between the notches. The fibers must lie parallel or perpendicular to the loading axis. Strain gages are placed at less than 45° in the direction of the shear plane in order to determine the shear extension. The ASTM method employs a double edge-notched, flat, rectangular specimen with two 90° notches cut at the edge mid-length with faces orientated at ±45° to the longitudinal axis. The notches extend to a depth of 20% of the specimen width (i.e. 4 mm). ASTM D 5379 recommends a notch root radius of 1.3 mm in order to minimize the shear stress concentration at the notch roots, and thus promote a more uniform shear stress distribution along the notch-root axis. The specimen has a length of 76 mm and a width of 20 mm with a specimen thickness between 3 and 4 mm. Specimens with a thickness less than 3 mm require adhesively bonded tabs (typically 1.5 mm thick) to prevent out-of-plane bending or twisting which could lead to premature failure. Local crushing, which can occur near the inner loading regions, can also be avoided by the use of tabs. Test specimen dimensions may be reduced if required.

2.8 Drilling Protocol

Drilling of a test laminate board was performed according to IPC Drilling protocol IPC-TM-650 2.6.24 A1-A4 configurations with 1000 holes per configuration.

3.0 Results

Figures 1 and 2 show the drill-hole surface profiles for laminate boards made from the non-toughened and toughened formulations, respectively. Figure 1 shows catastrophic failure in the drill-hole surface with brittle failure and fiber pull-out clearly visible. On the contrary, Figure 2 shows a smoother drill-hole surface for the toughened resin system. In our previous work, we performed a quantitative evaluation of the drill-hole surface roughness by mapping the topography of the drill-hole surface using profilometry. Results showed a significant difference in the drill-hole surface roughness with the non-toughened resin system showing a rougher surface topography. The surface defects observed with the non-toughened board are important because they have serious negative consequences on the downstream part fabrication and reliability processes.

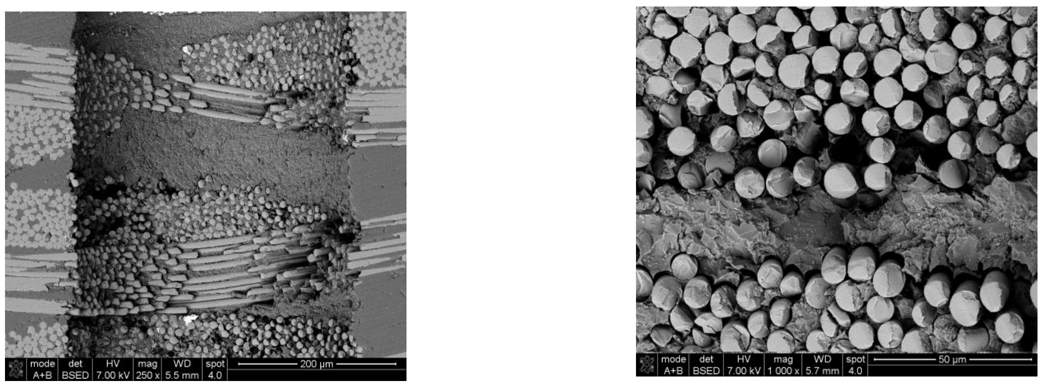

Figure 1. Drill-hole surface roughness for a laminate board made from a non-toughened resin showing a rougher drill-hole surface roughness characterized by brittle failure.

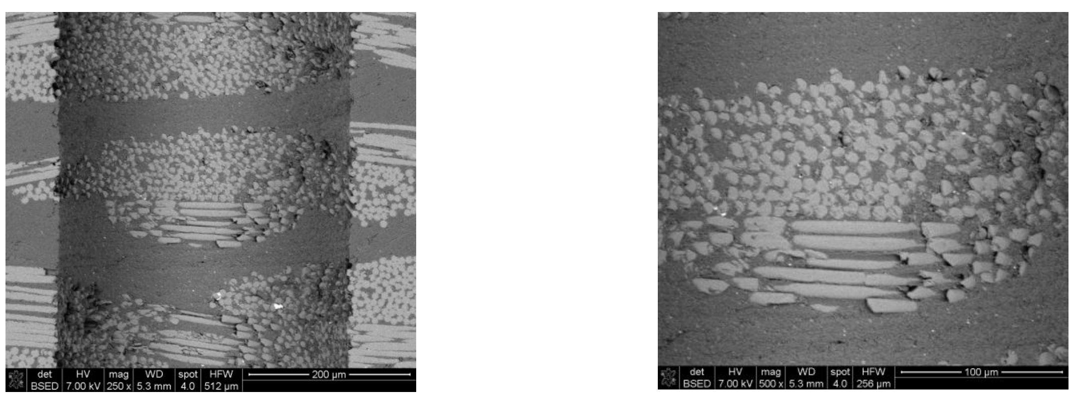

Figure 2. Drill-hole surface roughness for a laminate board made from a non-toughened resin showing a smoother drill-hole surface.

Generally, improvement in fracture toughness is accompanied by a decrease in other thermomechanical properties such as the glass transition or the thermal decomposition temperature. It is important therefore, that a toughener material added to a resin formulation imparts minimal adverse effects on thermomechanical properties if the high thermal stability characteristics of the material are to be exploited. Table 1 shows a summary of the thermomechanical properties of the high thermal stability resin system before and after toughening. It is shown that a 58% increase in the critical strain energy release rate was achieved when the toughener was added to the resin system. This was accompanied by a 54% improvement in interlaminar fracture toughness. These improvements were achieved with the minimal effect on all the other thermomechanical properties.

It was also shown that the failure mode of the laminate changed from cohesive to adhesive with the addition of FORTEGRA™ 351. Figure 3 shows laminate strips from a double-thick laminate separated during the interlaminar fracture toughness tests. The figure on the left shows the failure mode for a non-toughened laminate board. The white color of the laminate is indicative of resin removal showing glass only. In the figure on the left, partial exposure of the glass can be seen. This shows that crack propagated in the resin and thus leading to a cohesive failure mode. The figure on the right shows results for the toughened laminate board, where we see near perfect exposure on one piece of the laminate board. This is perfect evidence of a delamination failure mechanism. This was expected because as the resin became tougher, resistance to failure increased due to resistance to crack propagation in the bulk matrix. Therefore, though the interlaminar fracture toughness increases, the interface is comparatively more susceptible to crack propagation than the bulk resin.

Figure 3. Impact of toughener on interlaminar fracture toughness (G_{1C}) of a laminate board. Cohesive failure can be observed for the laminate strips on the left to which toughener was not added compared to the toughened laminate board on the right which exhibits adhesive failure.

Other important parameters of the dielectric material that can be adversely affected by the addition of toughening material are the electrical properties; specifically the dielectric constant D_k and the dissipation factor D_f. In Table 2 we show electrical properties of the test specimens with and without the toughener. Results show that electrical properties remained unchanged after the addition of the toughener. Therefore, the toughener does not contain ionic purities that would affect electrical properties of a resin formulation.

The laminate shear strengths for boards made using glass with the two finishes; Finish A and Finish B are shown in Figures 4 and 5 respectively, for toughened and non-toughened laminate boards. Figure 4 shows the shear strength for the Warp. It is shown that the shear strength improved with the addition of the toughener. Additionally, it was observed that the shear strength for the board made with the Finish B glass was higher than that observed with the Finish A. These results were also reproduced when the shear strength was measured in the Fill direction as well, as shown in Figure 5. Similar results were also observed for the tensile strength measurements as shown in Figures 6 and 7.

Table 1. The impact of toughener on thermomechanical properties for a high thermal stability resin system.

Metric	Phenolic-based Resin	Toughened Phenolic-based Resin (7.5 wt% toughener)
% Resin	41	42
Tg (C)	171	171
Td (5% wt loss) (C)	361	366
T288 (min)	25	23
CTE<Tg	63	69
CTE>Tg	274	277
UL-94 Rating	V0	V0
Cu Peel (lb/in)	7.63	7.92
Solder Dip @ 550F (%Pass)	100	100
G_{1C} (kJ/m^2)	0.41	0.76
K_{1C} (MPa.m$^{1/2}$)	0.68	1.17

Table 2. The effect of toughener on the dielectric constant of a resin formulation for electrical laminates. The electrical properties do not deteriorate subsequent to addition of the toughener to the formulation.

Test Frequency	Dielectric Constant (D_K)	
	Control	With Toughener
2 GHz	4.09	4.10
3 GHz	4.06	4.04
5 GHz	4.01	4.00
10 GHz	4.00	3.97

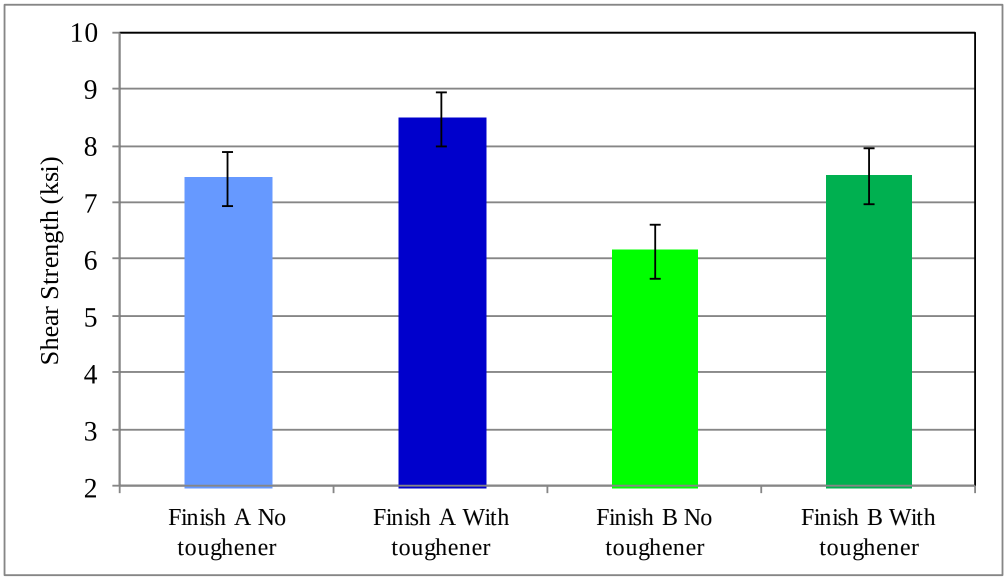

Figure 4. Shear strength (Warp) as a function of toughener and glass surface finish for a high thermal stability resin system.

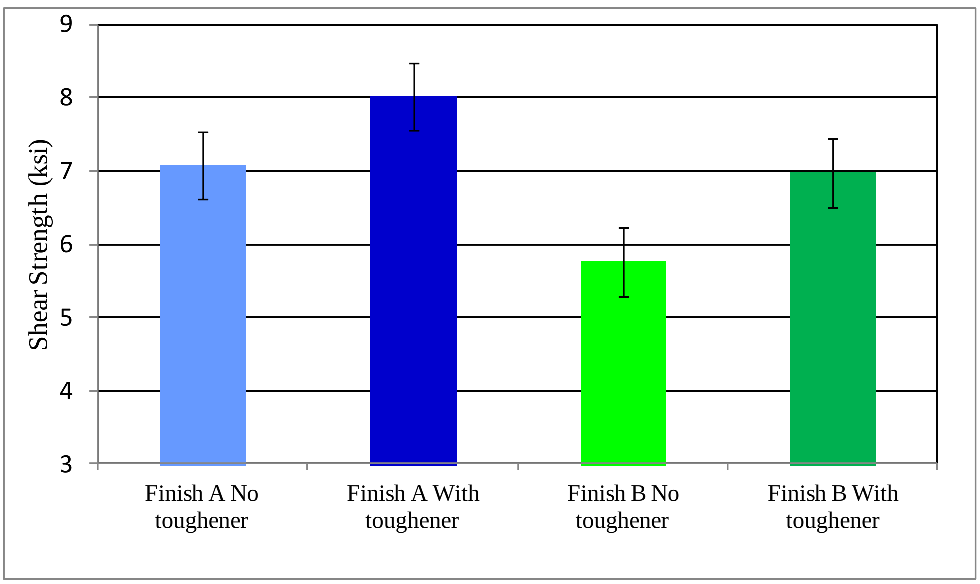

Figure 5. Shear strength (Fill) as a function of toughener and glass surface finish for a high thermal stability resin system.

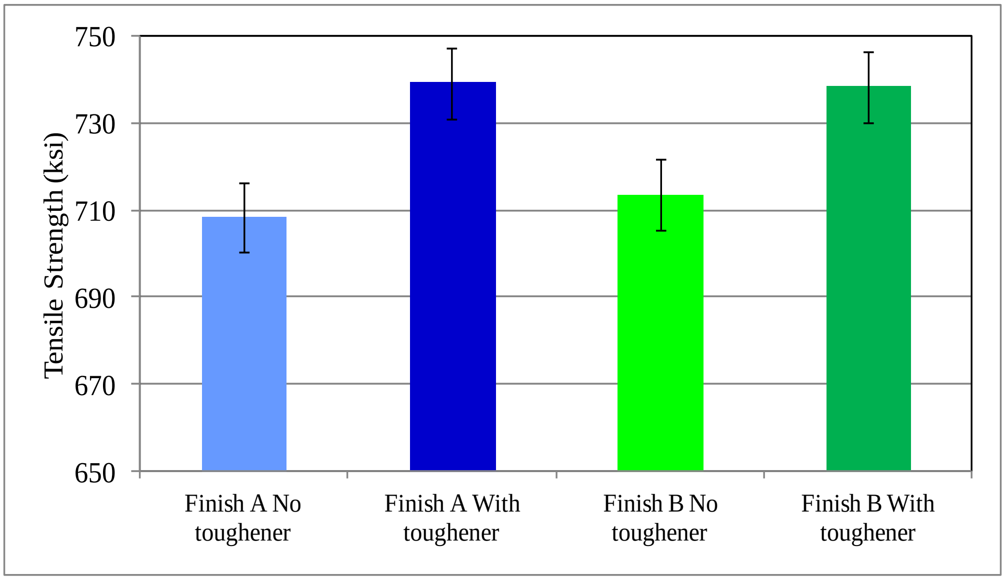

Figure 6. Tensile strength (Warp) as a function of toughener and glass surface finish for a high thermal stability resin system.

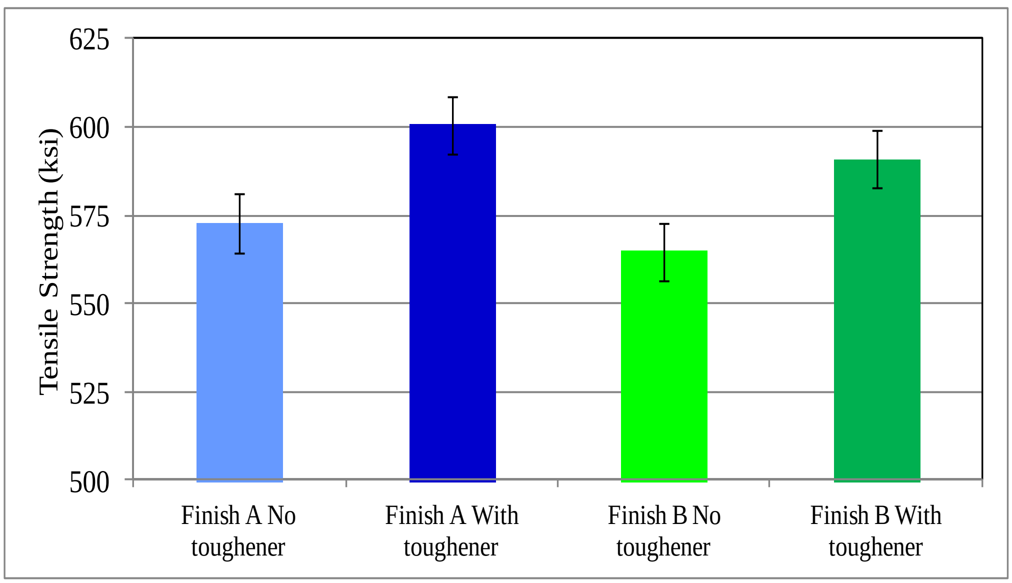

Figure 7. Tensile strength (Fill) as a function of toughener and glass surface finish for a high thermal stability resin system.

Figure 8 shows the impact of glass finish and the toughener on the copper peel strength of the laminate boards. For both glass finishes, the copper peel strength increases significantly with the addition of toughening material.

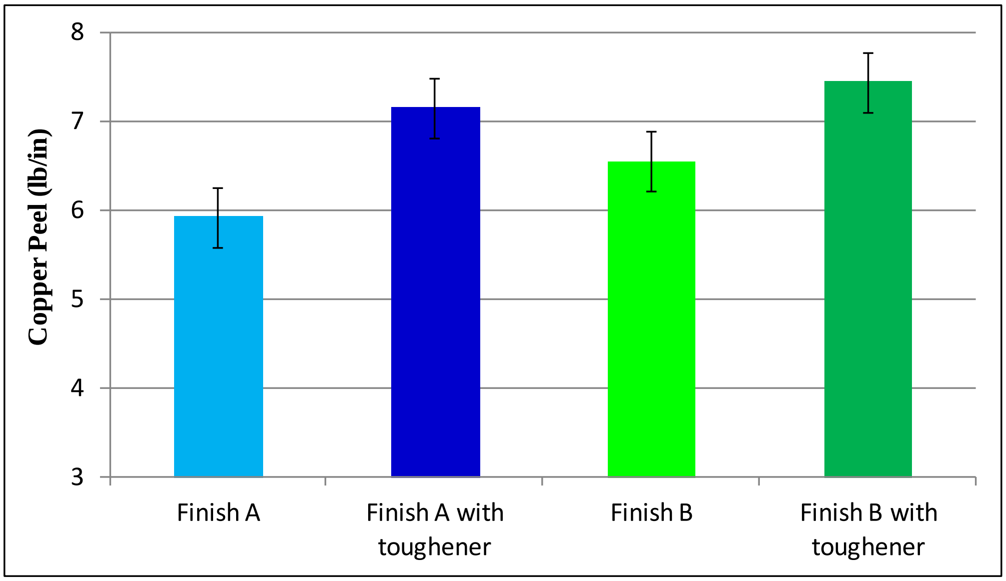

Figure 8. Copper peel strength as a function of toughener and glass surface finish for a high thermal stability resin system.

4.0 Conclusions

In this work, we studied the impact of the toughener and glass finish on the thermomechanical properties of a high thermal stability phenolic-based epoxy resin laminate board. Results showed that:

- The non-toughened laminate board suffered catastrophic brittle failure during drilling.
- Addition of the toughener to the resin formulation improved both the critical stress intensity factor and strain energy release rate by > 50%.
- The failure mode changed from cohesive to adhesive with the addition of the toughener; indicative of resistance to crack propagation in the bulk resin with the addition of the toughener.
- Addition of the toughener toughening material to the laminate formulation improved all the mechanical properties studied for both glass finishes.
- The laminate board with the Finish A glass exhibited superior mechanical properties in terms of the tensile and shear strengths over the Finish B glass laminate.
- Addition of the toughener to the laminate formulation did not affect electrical properties of the board.

5.0 References

[1]Lee, S-H., Kim, H., Hang, S., Cheong, S-K., *Comp. Sci. Technol*. 73 (**2012**) 1.
[2]Block, J.P., Henningsen, C.G., Tull, L. E., Printed Circuits Handbook, 3rd Edition, Chapter 10: Drilling and Machining, (1988).
[3]Hocheng, H., Tsao, C.C., *J. Mat. Proc. Technol.* 167 (**2005**) 251.

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Motivation

- Develop new toughening material to improve the fracture toughness of high thermal stability epoxy resin systems to sustain high mechanical stresses.

➢ No impact on other thermo mechanical properties.

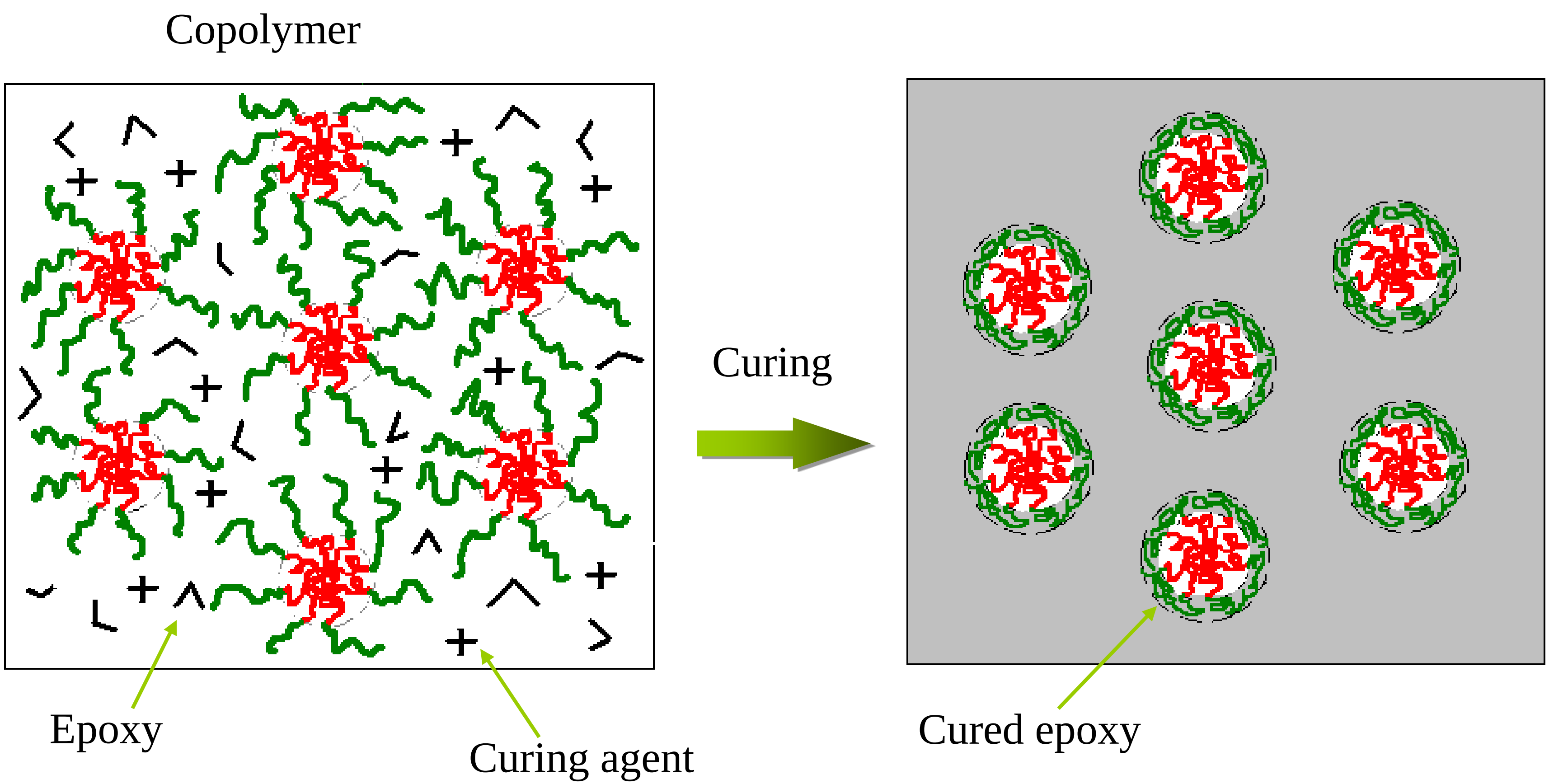
➢ No impact on electrical properties.

- Investigate the impact of two glass finish chemistries on laminate properties.

Outline

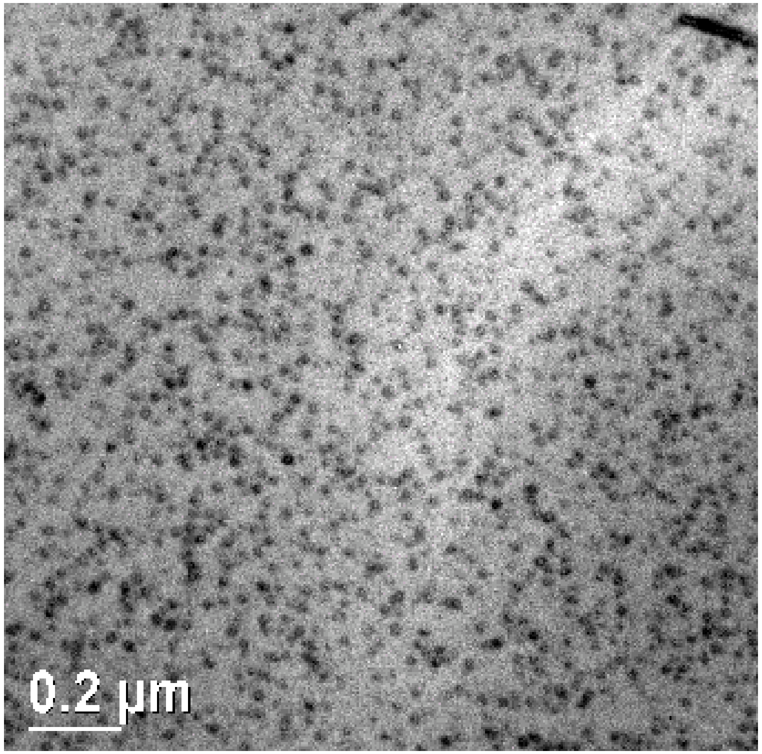
- Toughener Background
- Laminate Drillability and Drill-hole Surface Roughness
- Impact of FORTEGRA™ 351 on Thermomechanical Properties
- Impact of FORTEGRA™ 351 on Electrical Properties
- Impact of Glass Finish on Laminate Mechanical Properties
- Summary

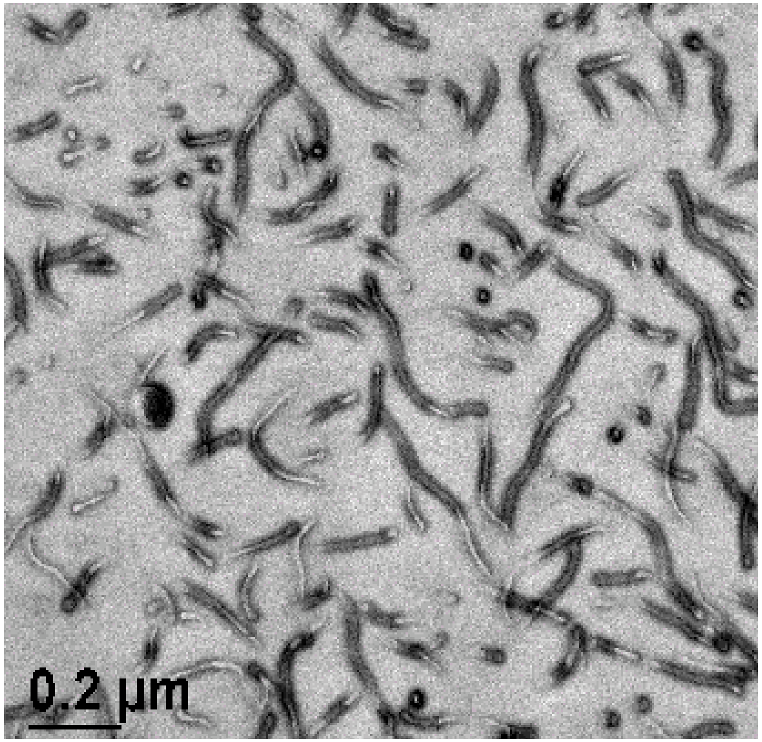
Background - FORTEGRA™ 100



Amphiphilic block copolymer technology - self-assembles to discrete particles

Self-assembled Morphologies

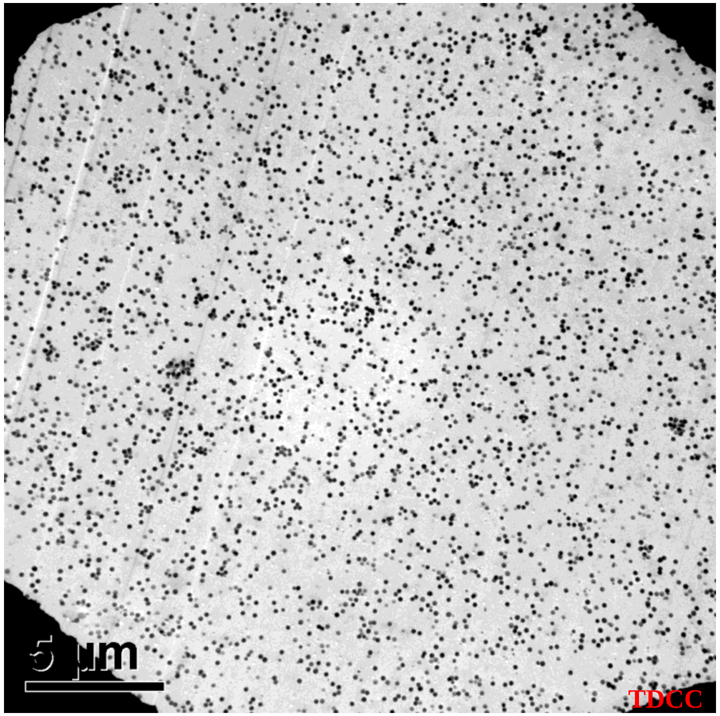


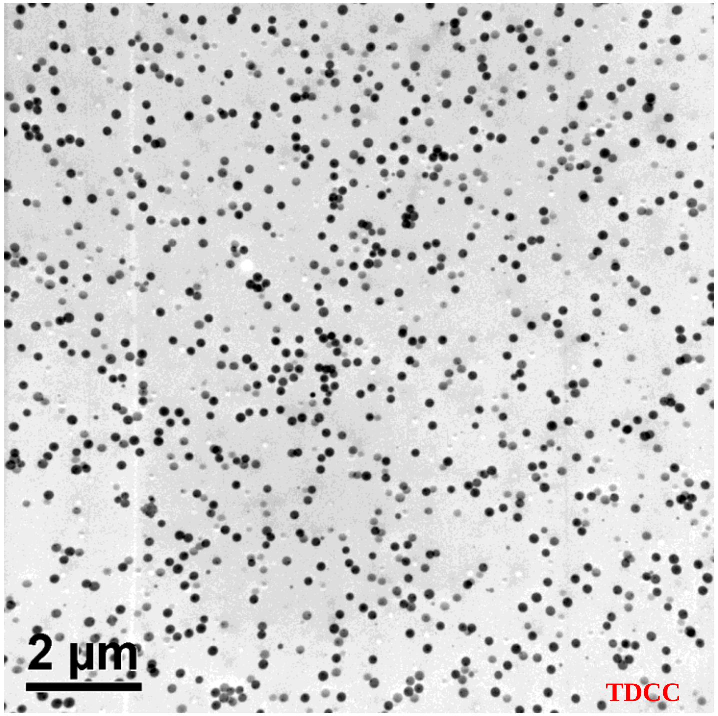


Hahn et al., *J. Polym. Sci., Part B: Polym. Phys*. Vol. 45, 3338 (**2007**)

Different morphologies can be generated different solvent selections - different impact on properties.

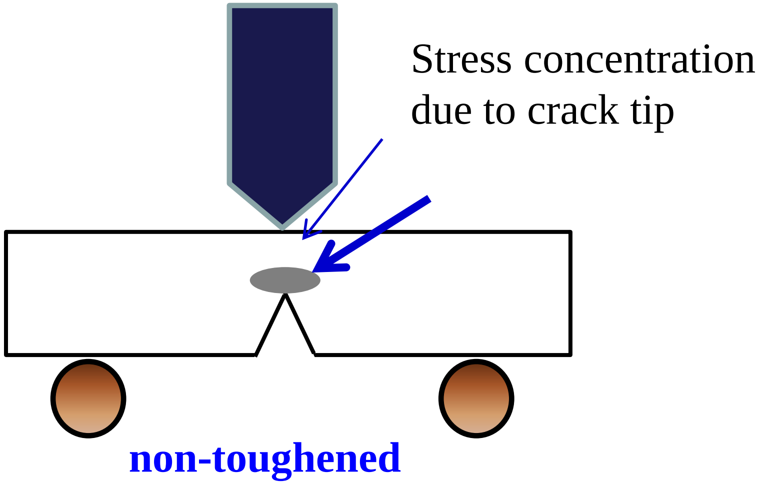
FORTEGRA™ 351

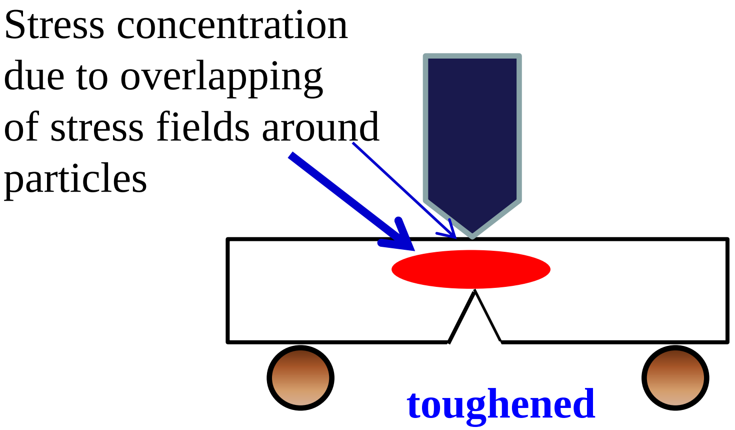




- Dispersed in a neat casting of an epoxy resin - excellent random distribution achieved.

The Toughening Mechanism

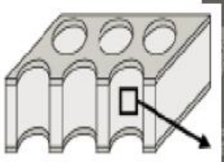


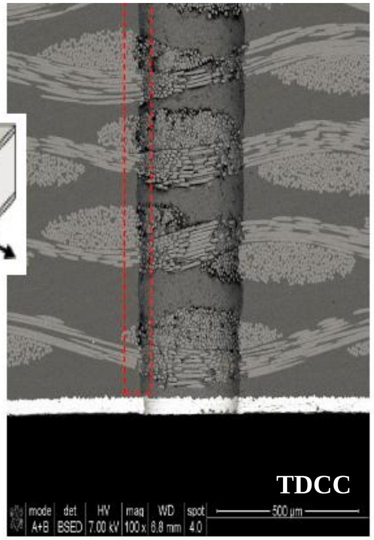


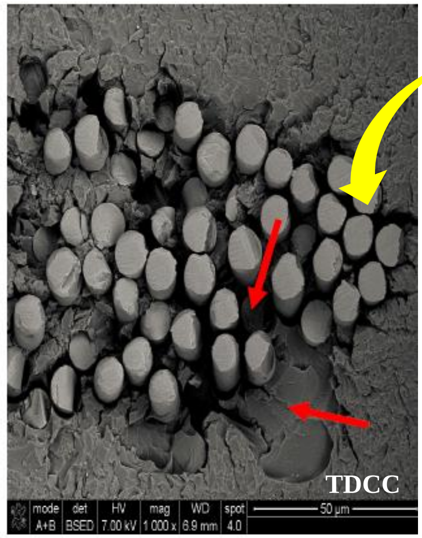
- Impact modifiers act as stress concentrators.
- Overlapping of stress concentration volumes around modifiers allows dissipation of impact energy in a larger polymer matrix volume.
- Dissipation of impact energy in a larger volume results in resistance to fracture – toughening.

Impact of Toughening on Brittle Resins

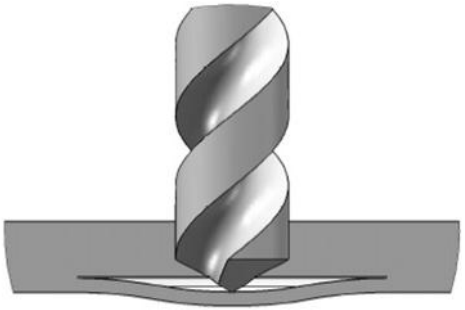
Non-toughened



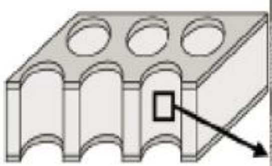


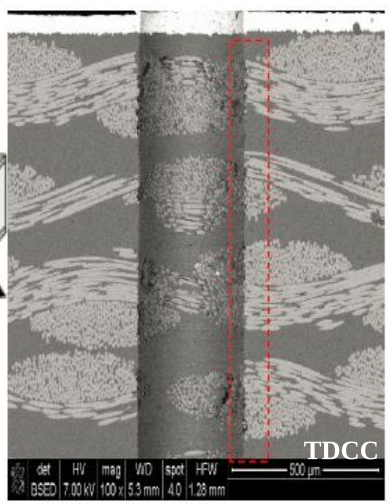


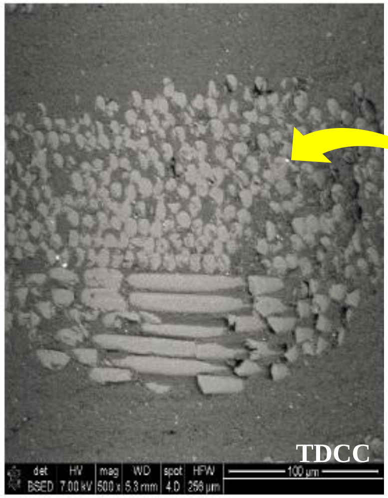
Extensive cracking observed around fibers.



Toughened







$$F_A = \pi \left[\frac{8 G_{IC} E h^3}{3\left(1 - \upsilon^2\right)} \right]^{\frac{1}{2}}$$

Hocheng et al., J. Mat. Proc. Technol. 140 (2003) 335

Smoother drill-hole surface observed subsequent to Toughening.

Thermo-mechanical Properties

Metric	Phenol-Novolac Resin (Control)	Phenol-Novolac Resin (with 7.5 wt% FORTEGRA™ 351)
Laminate Thickness	1.62	1.56
Tg (^{0}C)	171	171
Td (5% wt loss) (^{0}C)	361	366
% resin	41	42
T288 (min)	25	23
CTE<Tg	63	69
CTE>Tg	274	277
UL-94 Rating	V0	V0
Water Uptake (%)	0.30	0.40
Copper Peel Strength (lb/in)	7.63	7.92
Solder Dip @ 550 F (% Pass)	100	100
G_{1C} (kJ/m^2)	0.41	0.76
K_{1C} (MPa.m$^{1/2}$)	0.68	1.17

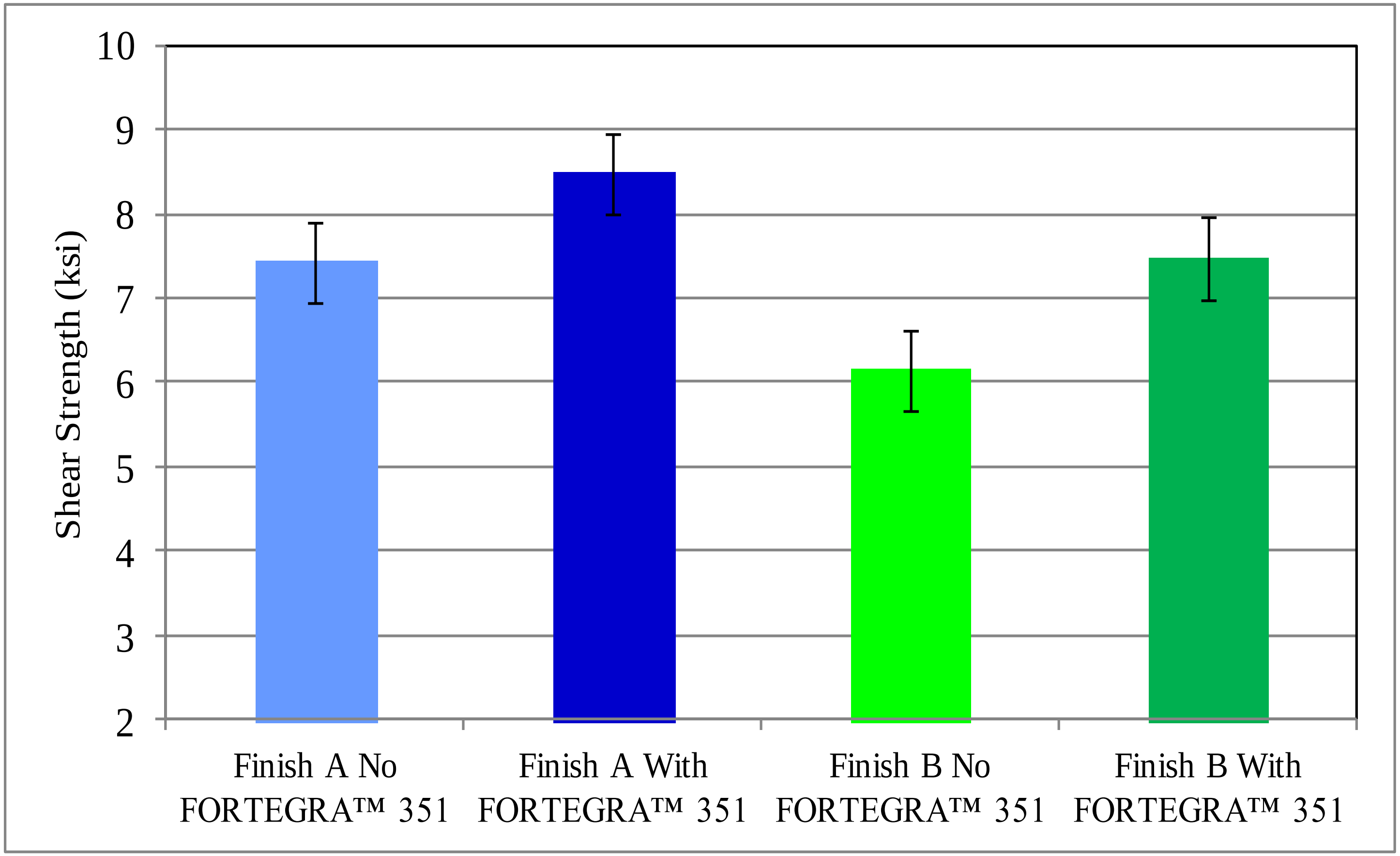
- Significant improvement in K_{1C} and G_{1C}.
- Very little impact on other thermo-mechanical properties.

Impact of FORTEGRA™ 351 on Electrical Properties (Dielectric Constant, D_K)

Test Frequency	Dieletric Constant (D_k)	
	Control	With FORTEGRA™ 351
2 GHz	4.09	4.10
3 GHz	4.06	4.04
5 GHz	4.01	4.00
10 GHz	4.00	3.97

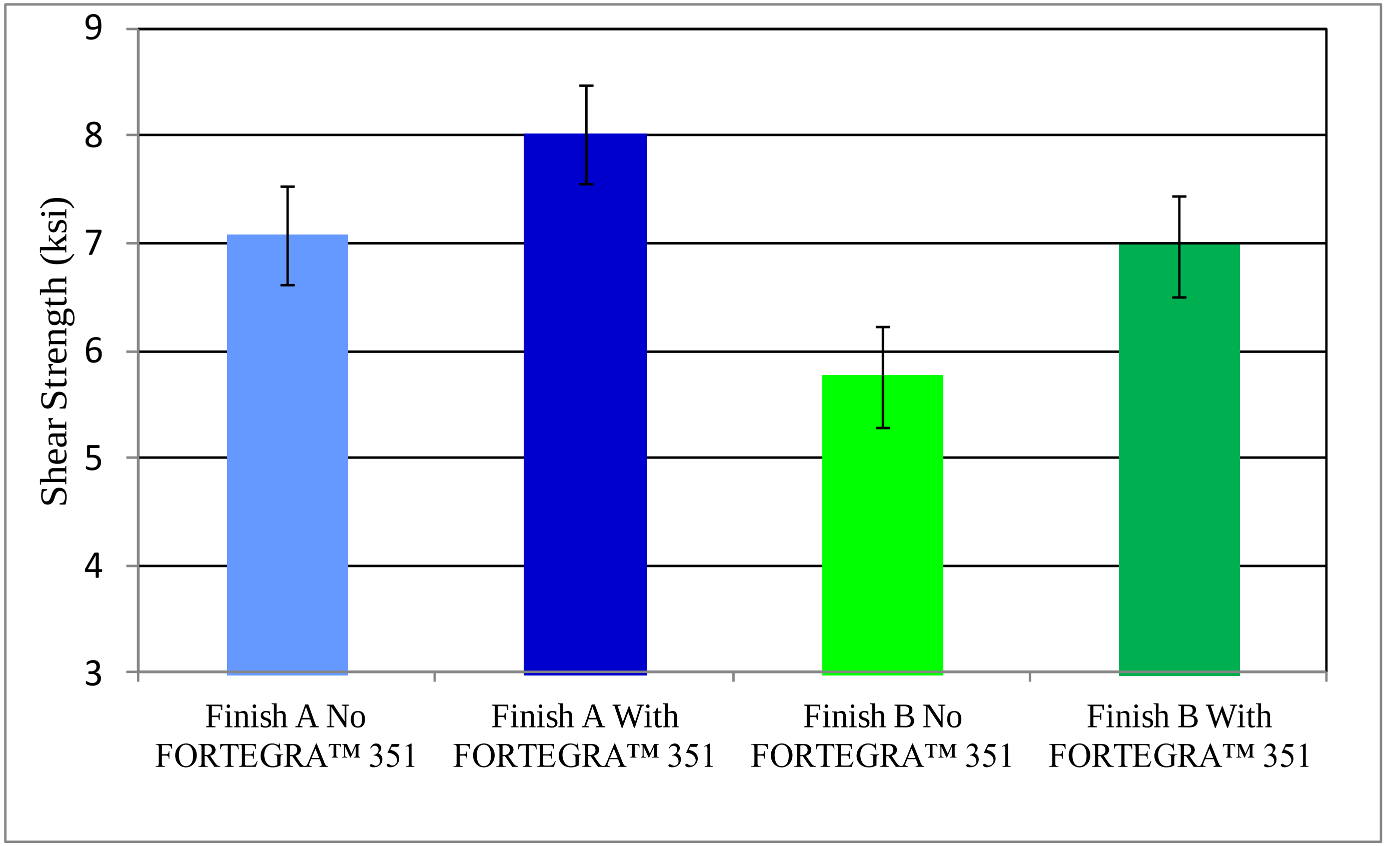
FORTEGRA™ 351 does not affect the dielectric constants of a base resin formulation for electrical laminates.

Shear Strength (Warp)



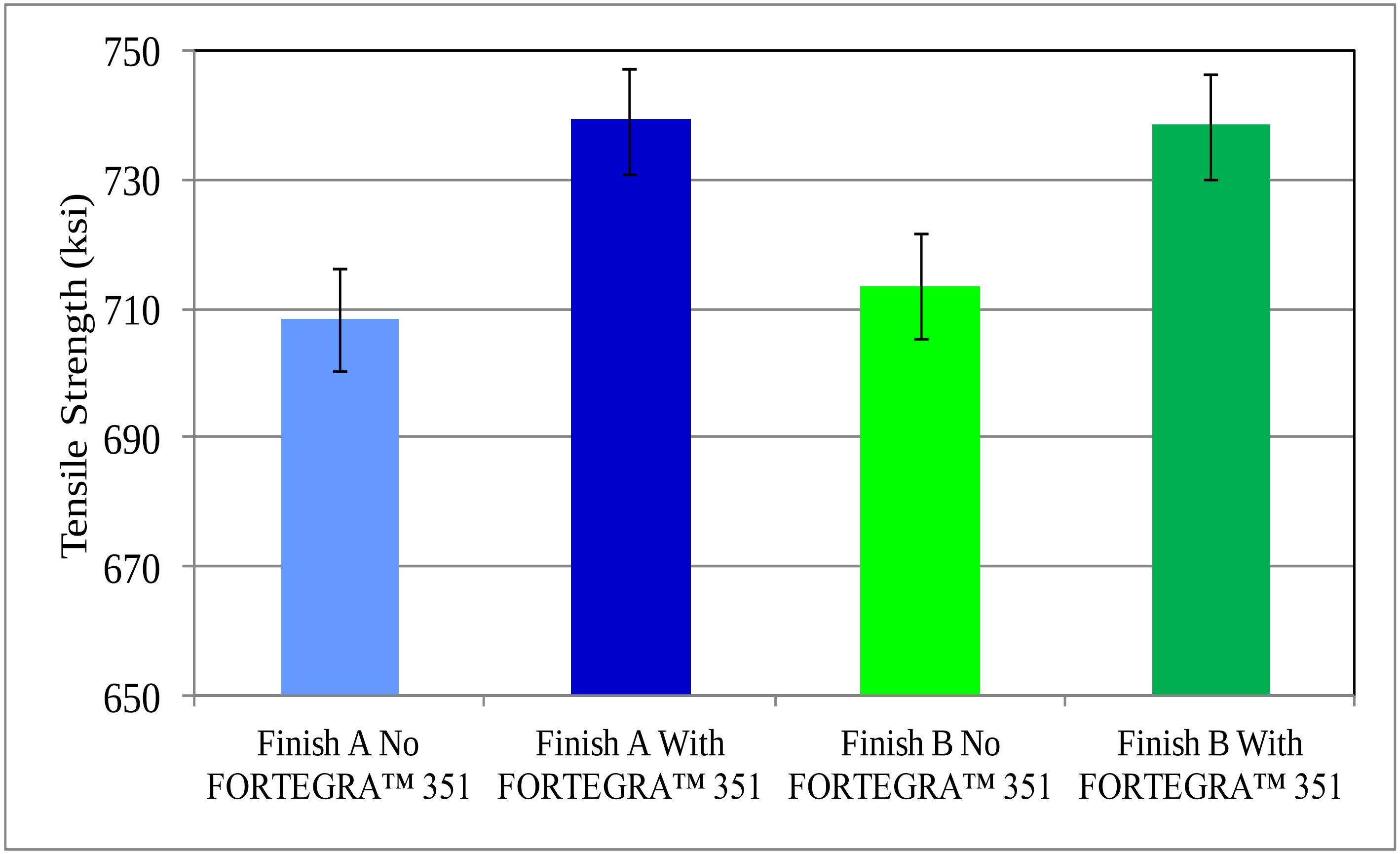
- The Finish A glass finish exhibits better shear strength than the Finish B finish.
- Further improvement in shear strength was observed when FORTEGRA™ 351 was added.

Shear Strength (Fill)



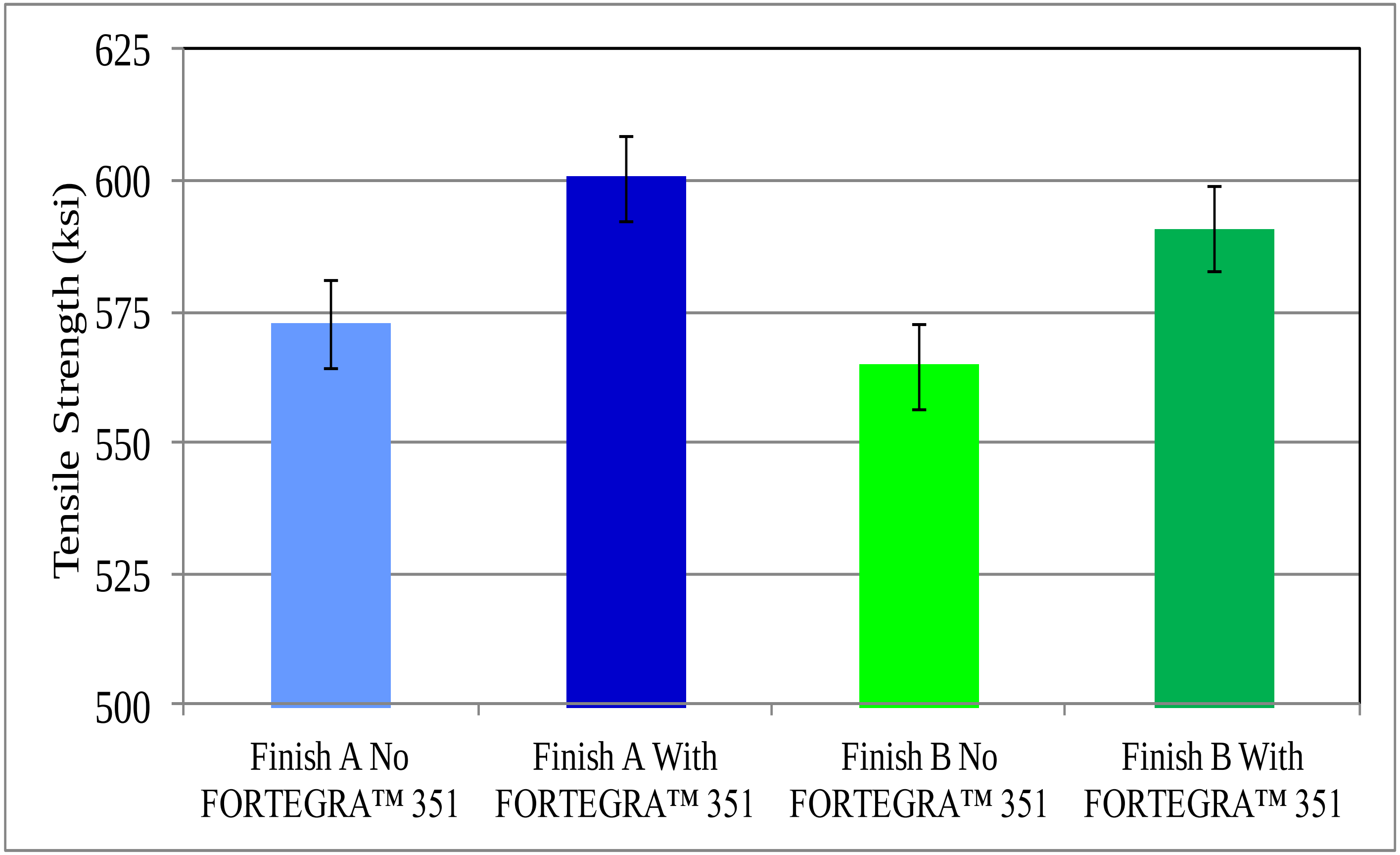
- The Finish A glass finish exhibits better shear strength than the Finish B finish.
- Further improvement in shear strength was observed when FORTEGRA™ 351 was added.

Tensile Strength (Warp)



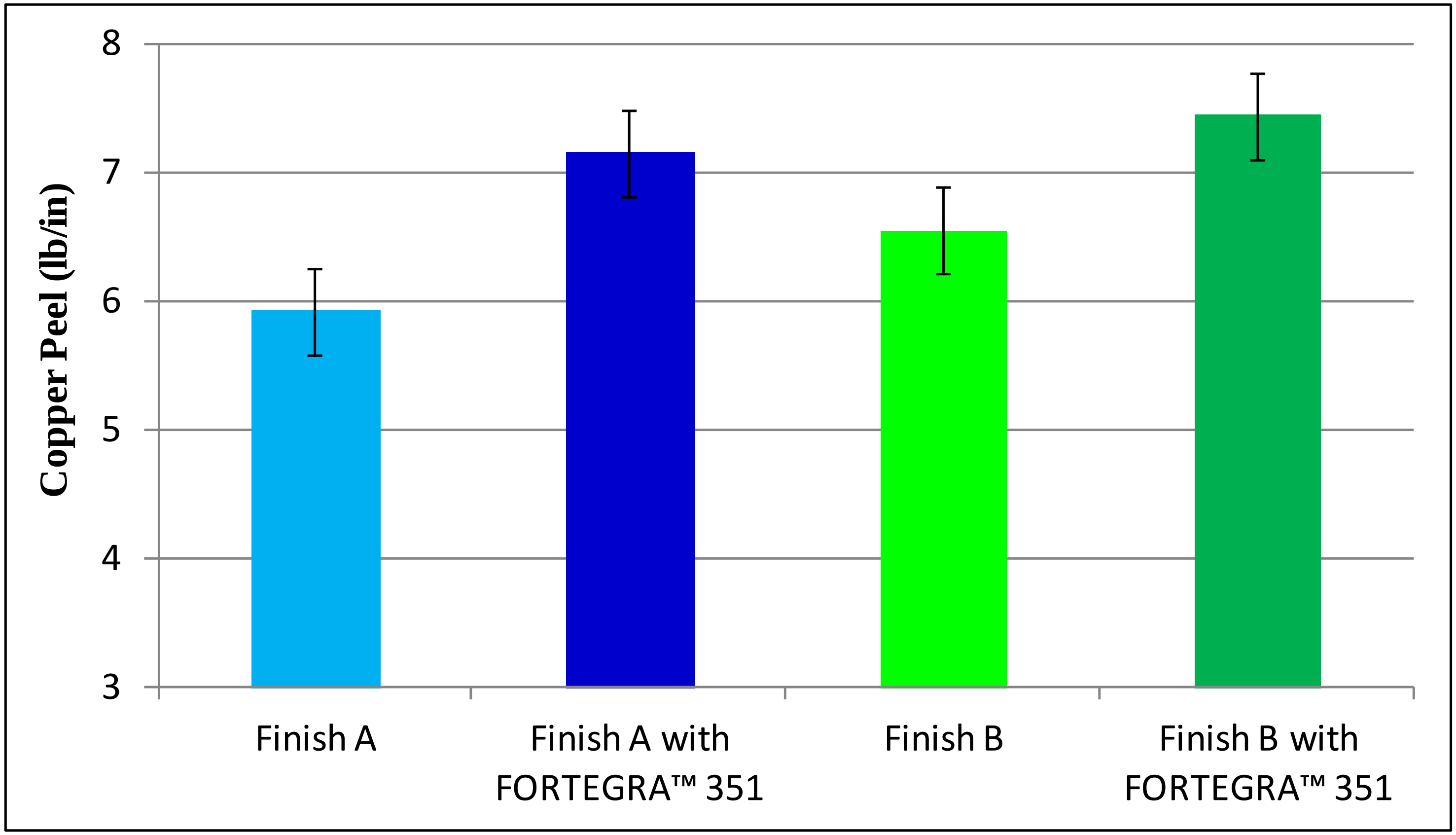
- Not much difference in tensile strength between the Finish A and Finish B glass finishes.
- Improvement in tensile strength was observed when FORTEGRA™ 351 was added.

Tensile Strength (Fill)



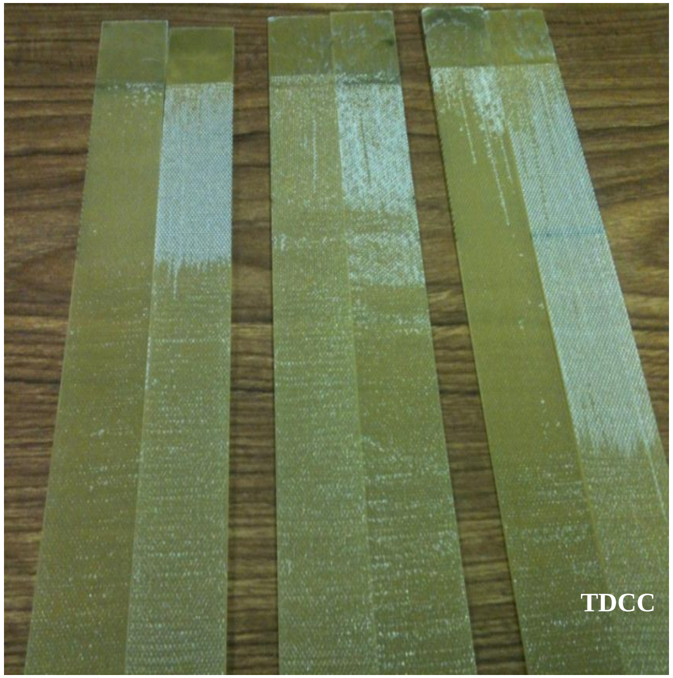
- Not much difference in tensile strength between the Finish A and Finish B glass finishes.
- Improvement in tensile strength was observed when FORTEGRA™ 351 was added.

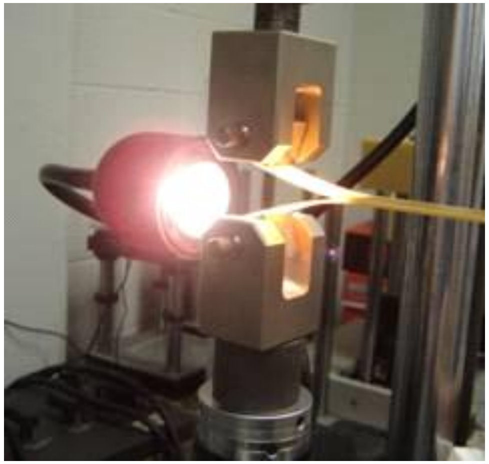
Copper Peel Strength

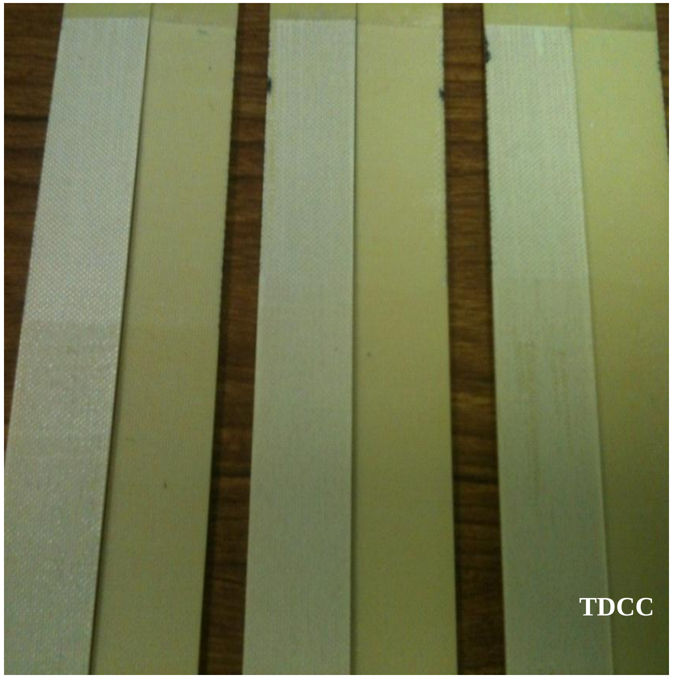


- The Finish B glass finish exhibits better copper peel strength than the Finish A finish.
- Further improvement copper peel strength was observed when FORTEGRA™ 351 was added.

Failure Mechanism (ILFT)







Non-toughened

Toughened

- With the addition of FORTEGRA™ 351:
  - ➢ adhesive strength improves (G_{1C})
  - ➢ failure mode changes from cohesive to adhesive.

Summary

- Brittle failure was observed subsequent to drilling a high thermal stability resin formulation.
- FORTEGRA™ 351 improves fracture toughness (K_{1C} and G_{1C}) without decreasing thermal properties.
- Drill-hole surface quality significantly improves with the addition of FORTEGRA™ 351 to the epoxy formulation.
- A cohesive to adhesive failure mechanism in the laminate was observed subsequent to addition of FORTEGRA™ 351.
- The laminate board with the Finish A glass-finish exhibited superior mechanical properties in terms of shear strength over the Finish B glass-finish.

Materials Availability

- The FORTEGRA™ 351 and the Finish A glass-finish are commercially available materials.