

Toughened Laminates for Printed Circuit Boards: Correlation of Drillability to Material Properties

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Abstract

With the miniaturization of electronic devices¹, the need for more versatile materials to make these devices increases. Coupled with the gradual removal of lead-based solders², thermal stability of modern electronics materials is necessary to withstand high rework temperatures. Alternative non-lead solders such as the tin-silver-copper (SAC) solder increase rework temperatures by about 30-40°. New chemistries that increase the glass transition (T_g) and thermal decomposition temperatures (T_d) have been developed to maintain the reliability of devices such as printed circuit boards (PCBs) and interconnect (IC) substrates during downstream assembly and rework processes. By increasing the crosslink density of a thermosetting material, higher T_g s are attained. The higher crosslink densities are achieved by increasing the functionality of the resins and hardeners. High crosslink densities are achieved at the expense of brittleness for these materials. During part fabrication of PCBs and ICs, circuitry is completed by copper-plated drill-holes between the different layers of the laminates. Currently, these drill-holes are predominantly mechanically drilled into the laminate. Drilling of brittle laminates is problematic because of problems associated with cracking, delamination, and drill-bit wear and breakage. Although the drilling equipment, drill bits, and drilling parameters can be optimized to minimize such issues, additional efforts are desirable to improve the drillability of the PCBs and ICs. Toughening materials are being incorporated into the resin formulations to improve drillability.

In this work we report results from a study on incorporating pre-formed toughening materials into high crosslink density phenolic cured resin formulations and the effect of the toughener on thermomechanical properties, toughness and drillability of the electrical laminates. The objective of the current work is to provide a toolbox that will help correlate the thermomechanical properties of the resin formulations to the drillability performance of the corresponding PCBs. Such a correlation is presently absent. These correlations will speed the new materials evaluation process relative to the drillability performance without the expensive and time-consuming process of performing extensive drilling studies.

1.0 Introduction

To improve the thermal stability (increase T_g and T_d) of epoxy-based electrical laminate formulations, phenolic cure chemistry has been employed. Use of phenolic hardeners increases the crosslink density significantly and thus increasing both the glass transition and thermal decomposition temperatures. With the high crosslink densities comes brittleness. The brittleness is important because it affects part fabrication and reliability. In the fabrication of electronic parts such as printed circuit boards, holes are drilled into the copper-clad multi-ply boards and later the drilled holes are plated with copper. Currently, these drill-holes are predominantly mechanically drilled. The drilling of these holes causes defects like cracks, delamination, and debonding in a brittle laminate board. Furthermore, the drilling of brittle laminates results in high drill bit wear and breakage. 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.

High-speed part fabrication methodologies are employed in the fabrication of modern electronic devices. For example, drilling of laminates is performed at very high cutting speeds and feed. The high cutting speeds induce high temperature build-up³ in the drill hole as shown in Figure 1. Temperatures in the vicinity of the resin glass transition can be easily reached. The temperature rise is important because it negatively affects drill-hole quality as shown in Figure 2³ where the quality of the drill-hole surface declines with increasing drill-bit temperature.

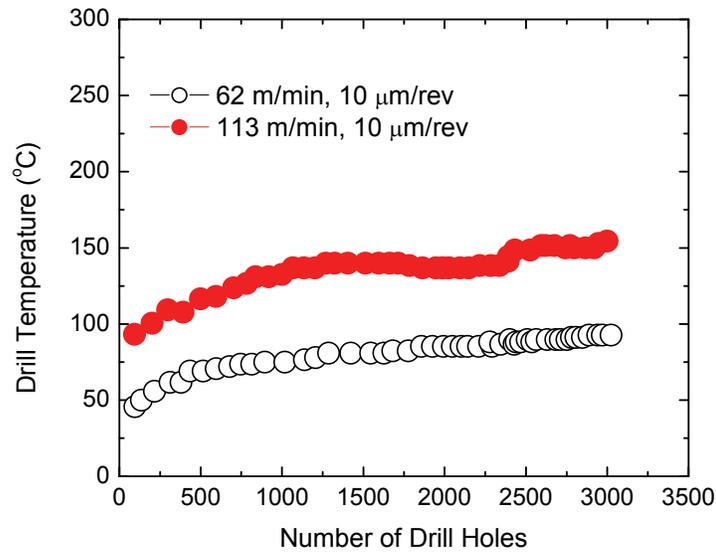


Figure 1. Increase in drill temperature at two cutting speeds as a function of number of drill-holes at a constant feed rate (digitized data from Nagawa, et al)³

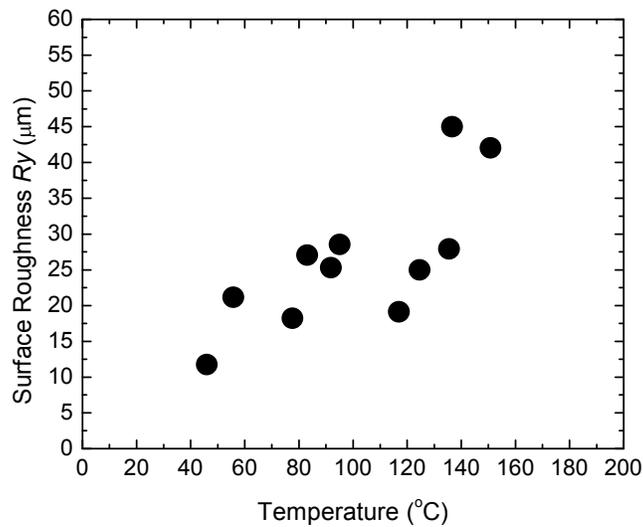


Figure 2. Deterioration in drill-hole surface quality with increasing drill temperature (digitized data from Nagawa, et al)³.

In this work we report the toughening effect of proprietary Dow toughening materials on thermomechanical properties on proprietary high thermal stability Dow resin formulations. In the absence of an industry wide accepted quantitative evaluation methodology for drill-hole defects, qualitative evaluation of the differences between the drill-hole surface roughness of a toughened laminate to that of a non-toughened laminate is presented. Presently, no standard metrics exist to benchmark good drillability, and moreover, to our knowledge, there is no work that has reported a correlation between resin toughness and good drillability. We report in this work our efforts to deliver such a correlation.

2.0 Experimental

2.1 Materials

Laminate boards were prepared from 8 B-staged prepregs. The prepregs were prepared on 7628 glass. The prepreg resin content was maintained at ~ 45 wt%. Subsequent to thermomechanical validation, a test vehicle was prepared and via fabrication performed. Boards were prepared from a non-toughened formulation and formulations toughened with preformed toughening agents. Drilling of through-holes was performed at Saturn Electronics, Romulus, MI.

The boards were drilled at a cutting speed of 110,000 rpm and a feed rate of 70 in/min at ambient conditions using a tungsten carbide drill-bit with a 0.0145" diameter.

2.2 Sample Preparation

The formulation of interest was prepared by blending the components in methyl ethyl ketone (MEK) and shaking until homogeneous. The toughener was pre-dispersed in MEK at 20% solids level using a Cowles blade at 2000 rpm. 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 Stoke 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 (2-methylimidazole) 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_{IC} 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. Thermal Expansion

A Thermal Mechanical Analyzer (TMA), TA Instruments Q400, was used to measure the coefficient of linear thermal expansion (CLTE) below and above T_g . Copper clad laminate samples are cut into ~9 mm x ~9 mm squares using a water cooled diamond tile saw. CLTE ($< T_g$ and $> T_g$) is obtained from the slope of the thermogram below and above T_g . The TMA was also used to determine the time to delamination at 288°C (T288). The time to delamination was determined as the elapsed time from when the temperature reached 288°C to when a sudden significant dimensional change (~100 μ m) occurred.

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.

3.0 Results

Figures 3(a, b) show the drill-hole surface for a phenolic-cured laminate without any toughening additive. The surface exhibits significant brittle failure that is characterized by fiber pull-out, debonding in the fiber-matrix interface, and resin fragmentation. Clearly, the material suffers significant stress under a mechanical force. The high rework temperatures of the lead-free solders would induce significant strain changes in the resin that would result in similar failure. The rough surface is problematic for copper plating because copper filaments can penetrate the cracks. Furthermore, cleaning chemicals and gases can be trapped in the crevices during plating and cause further catastrophic events such as debonding/delamination over time. For a board whose integrity is so compromised during drilling, further problems can occur during rework. Figure 3 shows micrographs of the non-toughened control and Figure 4 shows the same material with various levels of toughener. Qualitatively, the drill-hole surface roughness does not seem to exhibit toughener loading dependence between these loading levels. However, the characteristic brittle failure observed with the non-toughened resin formulation is absent: no fiber pullout or delamination/debonding in the fiber-resin interface is observable. Clearly, the inclusion of toughening agents in the formulation dissipates stress induced by the drilling force. The efficient stress dissipation helps to maintain the integrity of the laminate.

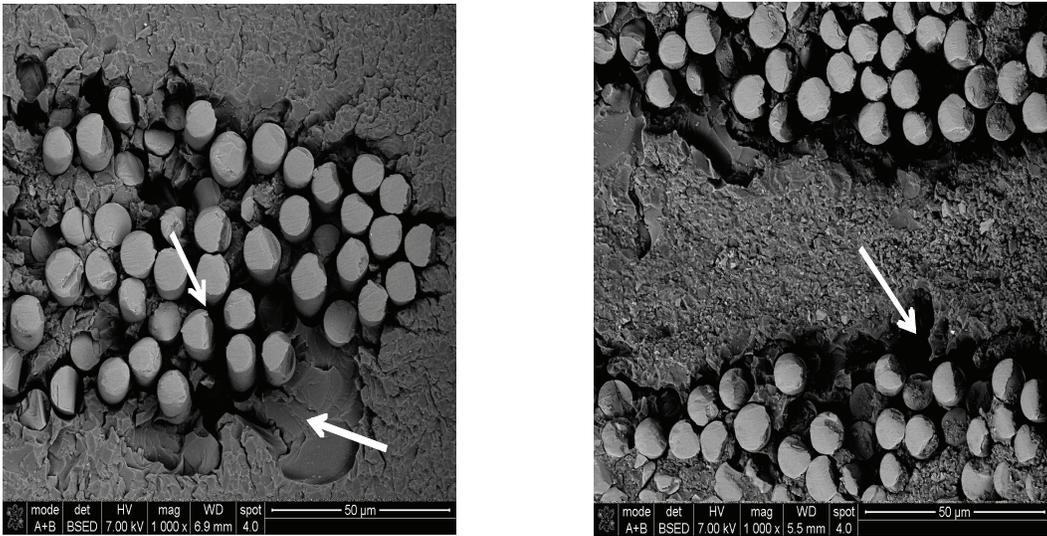


Figure 3(a, b). Drill-hole surface roughness of a non-toughened phenolic cured laminate formulation. Fiber pullout, debonding, and brittle failure are clearly visible as indicated by the white arrows.

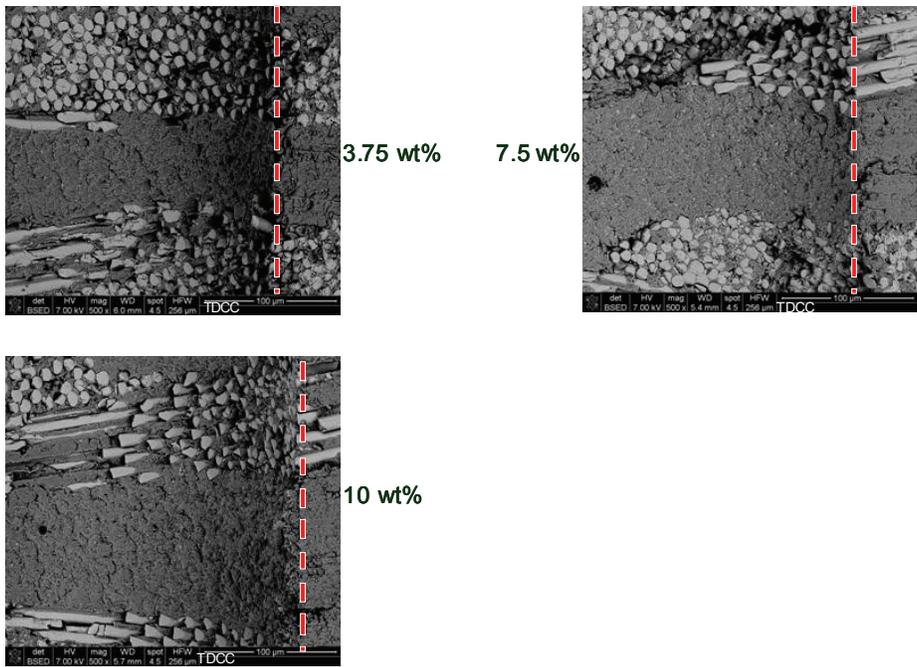


Figure 4. Drill-hole surface roughness for a phenolic-cured laminate board showing the dependence of toughener loading on drill-hole surface roughness.

Figure 5 shows moisture uptake by the resin subsequent to a pressure cooker test (at 124°C) as a function of toughener loading. Results show that the moisture uptake increases with increasing toughener loading. It is also observable that the moisture uptake reaches a constant value above a toughener loading of 3.75 wt%. Importantly, even at the highest toughener loading of 10 wt%, the observed moisture uptake is below the maximum allowable target of 0.5 wt% typically necessary to pass the subsequent solder immersion test.

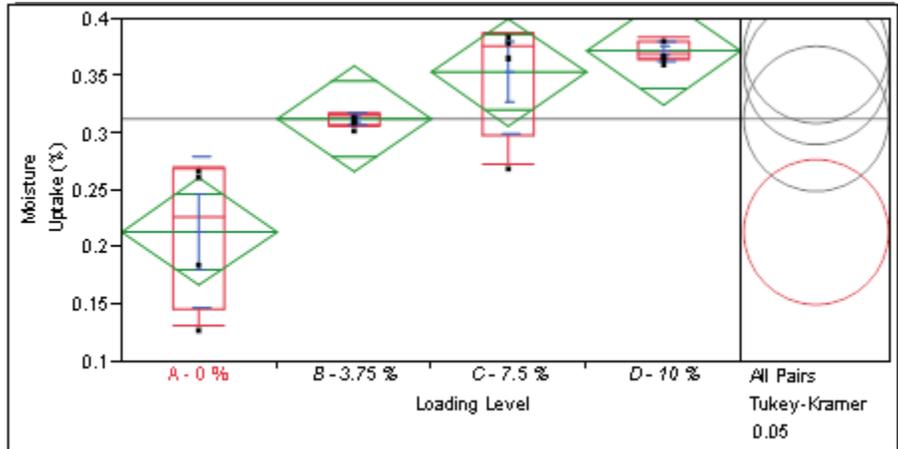
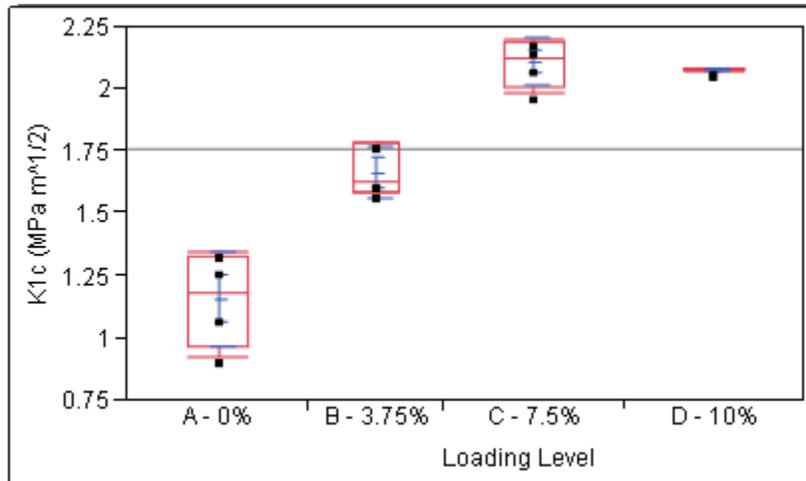


Figure 5. Moisture uptake as a function of toughener loading

Figure 6 shows the effect of toughener loading on the critical stress intensity factor (K_{1C}). The fracture toughness increases with increasing loading of toughening agent. Between a toughener loading of 3.75 – 7.5 wt % the fracture toughness attains a plateau above which no increase in fracture toughness is observed with increasing toughener loading. The optimized toughener loading is therefore in the vicinity of 3.75 wt%.



Figures 6. The dependence of fracture toughness (K_{1C}) on toughener loading.

Figure 7 shows the dependence of the interlaminar fracture toughness (G_{1C}) on toughener loading. With increasing toughener loading, the interlaminar fracture toughness (strain energy release rate) increases. However, it is also observed that the interlaminar fracture toughness asymptotes at 3.75 wt% toughener loading. Above this value there is no corresponding increase in interlaminar fracture toughness with increasing toughener loading. It was also observed that the failure mode for the sample loaded with 3.75 wt% of toughener and below was cohesive. However, above 3.75 wt% toughener loading, the failure mode was adhesive. Therefore, the 3.75 wt% toughener loading lies in the vicinity of a transition from cohesive to adhesive failure. This result also clearly demonstrates that with addition of toughener to the sample, toughness increases as shown by the transition of the failure mode to adhesive indicating that the fiber-matrix interface is a region of stress concentration and not the bulk resin region with dispersed toughener particles.

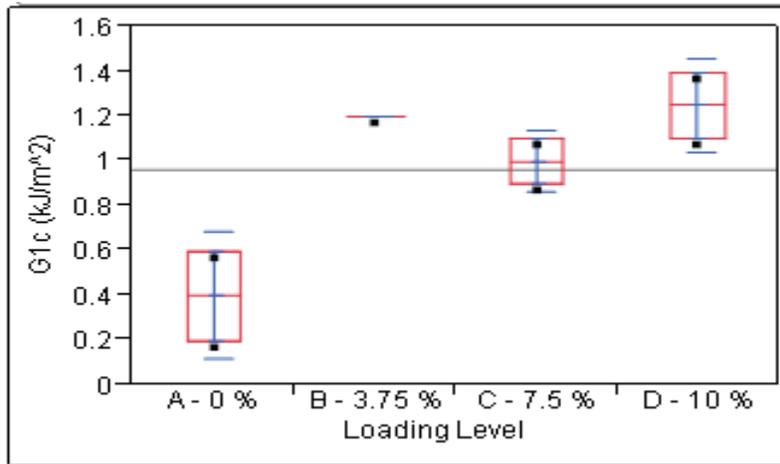


Figure 7. Dependence of interlaminar fracture toughness (G_{1c}) on the loading level of toughening agent.

Table 1 shows a summary of laminate level data of the thermomechanical properties of a toughened laminate compared to those of the control. Clearly, the incorporation of toughening particles into the high thermal stability laminate formulation does not induce depreciation of thermomechanical properties. In fact, despite a small drop in the glass transition temperature, an improvement in thermomechanical properties is observed. Importantly also, the material passes the UL 94 flammability test.

Table 1. Summary of the thermomechanical properties of the toughened laminate compared with those of the non-toughened control.

Parameter	Control	Toughened Sample
Toughener Loading Level (wt%)	0	3.75
Laminate Thickness (mm)	1.57-1.70	1.37-1.60
T_{g3} ($^{\circ}$ C)	177	173
T_d (5wt% loss) ($^{\circ}$ C)	363	365
Resin Content (%)	42.1	41
T288 (min)	30.2	26.2
CTE $<T_g$ (ppm/ $^{\circ}$ C)	60	35
CTE $>T_g$ (ppm/ $^{\circ}$ C)	260	228
Copper Peel (lb/in)	7.63	7.92
Moisture Uptake (%)	0.25	0.2
Solder Dip 550 F (% Pass)	100	100
UL 94 Rating	V-0	V-0

4.0 Conclusions

A toughening material was incorporated into a high thermal stability phenolic cured epoxy resin formulation and laminate level data evaluated. Results show that:

- The non-toughened laminate exhibits brittle failure subsequent to drilling.
- The laminate with toughener material is tougher and devoid of brittle failure subsequent to drilling.
- Moisture uptake does not exhibit a loading dependence above 3.75 wt% toughener loading.
- Critical stress intensity factor (K_{1c}) asymptotes to a plateau above 3.75 wt% loading of toughening aid.
- Strain energy release rate shows a transition in the failure mode from cohesive to adhesive in the vicinity of 3.75 wt% toughener loading

A significant improvement in the fracture toughness is realized with the use of the toughening material employed which results in improved drillability. Additionally, the optimized loading level for this material in the high thermal stability epoxy resin formulation used in this study is in the vicinity of 3.75 wt%.

5.0 References

1. Charles Jr., H, *Johns Hopkins APL Technical Digest*, Vol. 26, No. 4 (2005)
2. Reid, P., *Printed Circuit Design and Fab*, 2008
3. Nakagawa et al., *Journal of Materials Processing Technology*, 191 (2007) 293

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Motivation

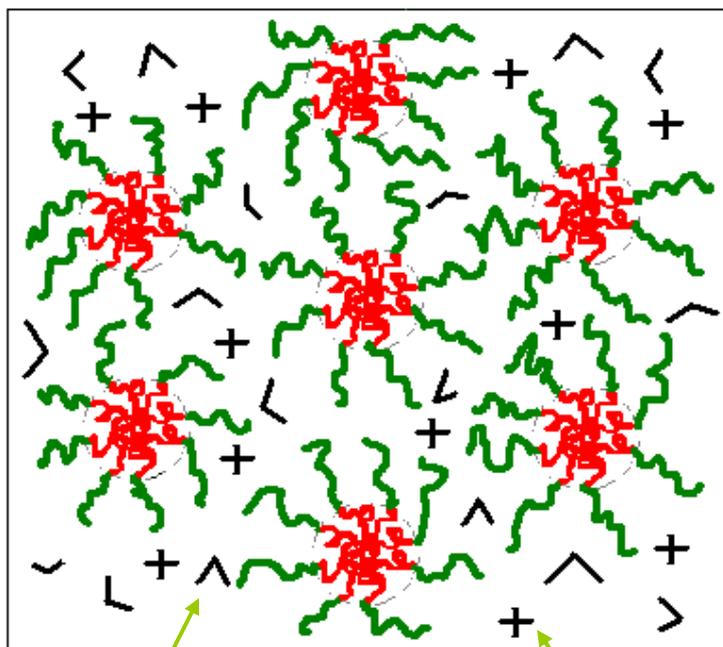
- Develop new phenolic cure chemistry for electrical laminates allowing for higher Tgs, higher decomposition temperatures to accommodate higher solder/reflow temperatures.
- However, phenolic-cured laminates are brittle and cause drill bit wear and breakage. In addition, the irregular hole-surfaces reduce the reliability of plated-through-holes.
- Therefore, develop a toughening package of benefit to the new products.

Outline

- Toughener dispersability
- Thermomechanical properties
- Drill-hole surface roughness (Qualitative)
- Conclusions

Background - FORTEGRA™

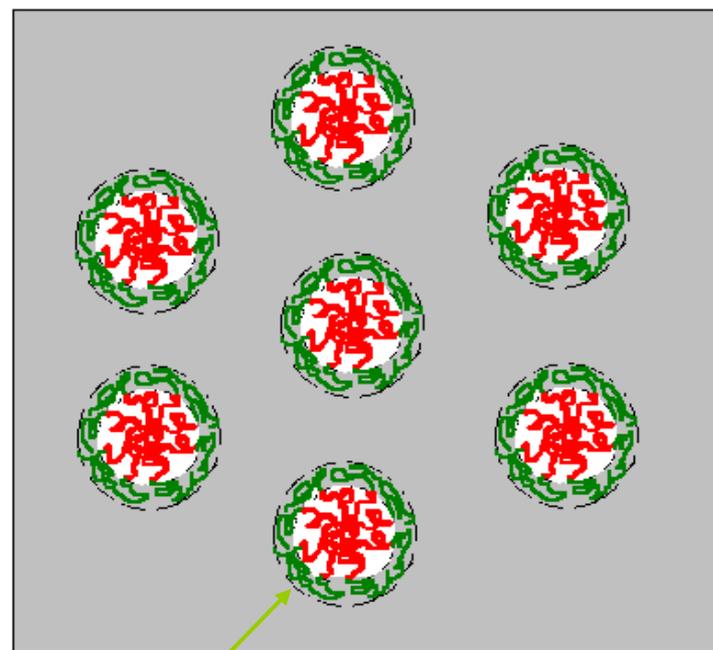
Copolymer



Epoxy

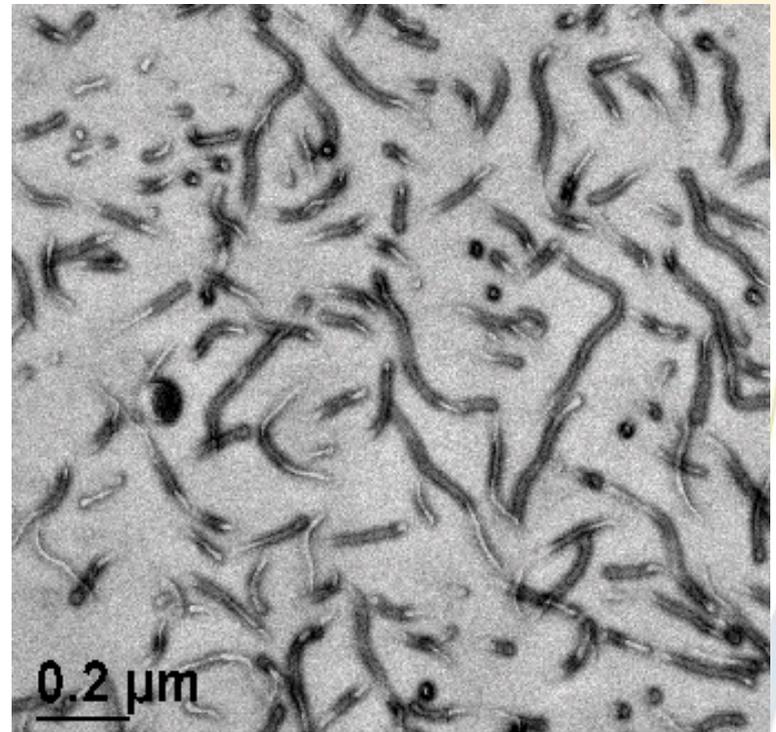
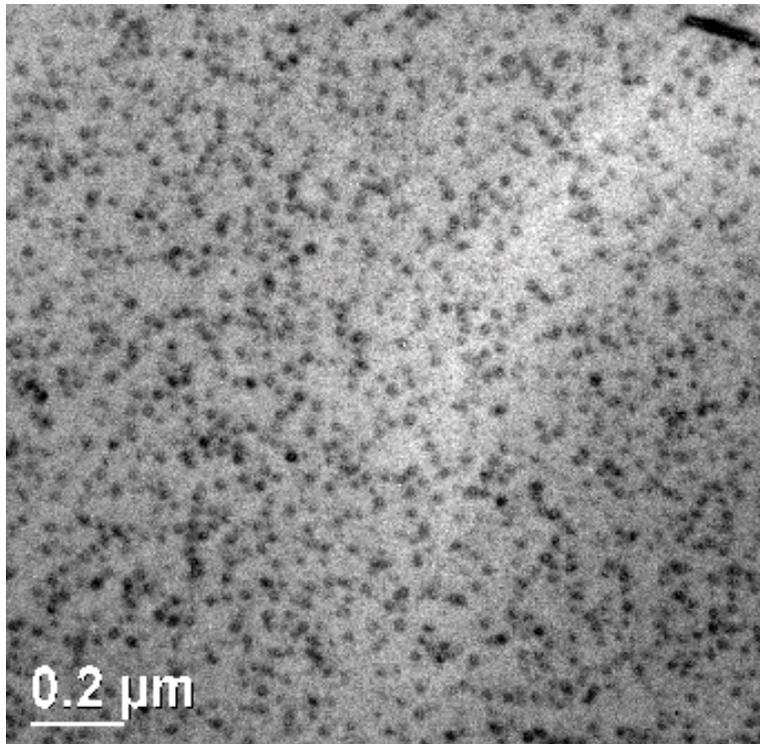
Curing agent

Curing



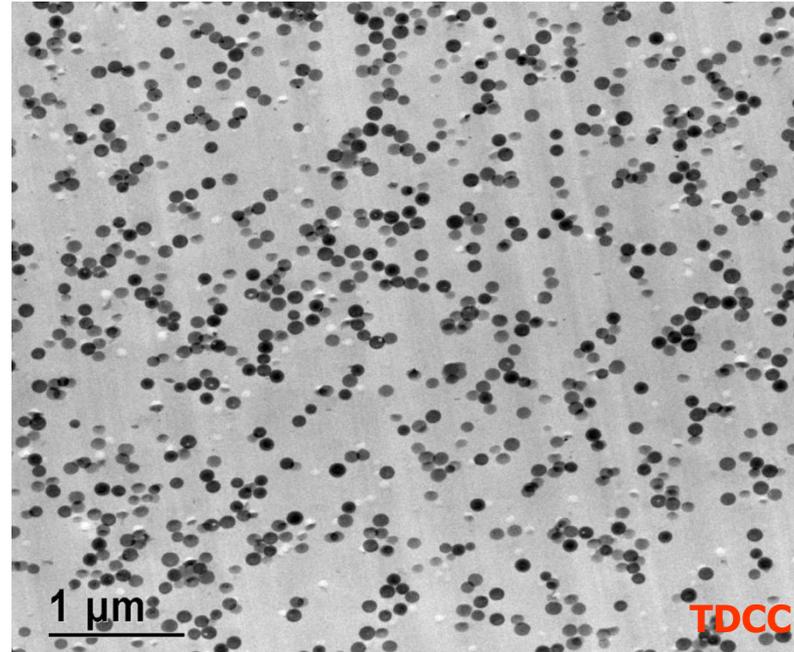
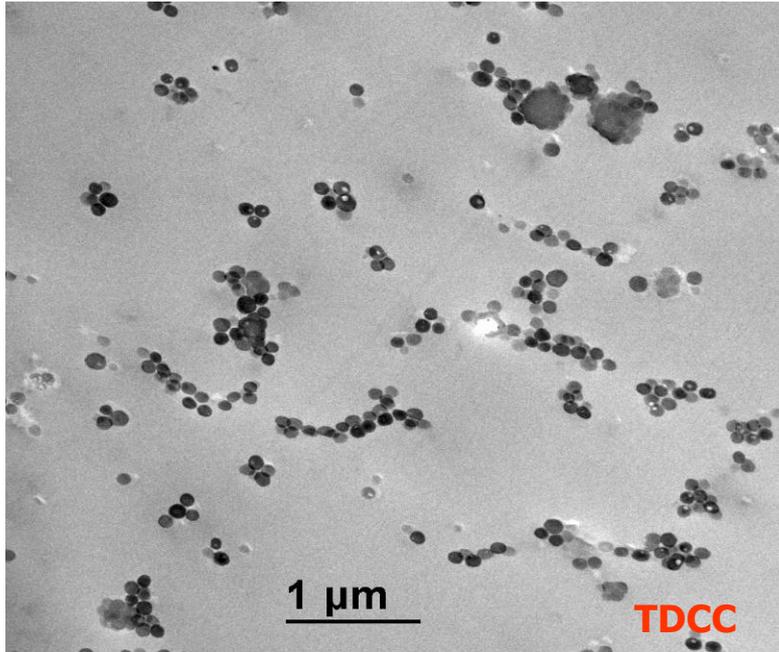
Cured epoxy

Self-assembled Morphologies

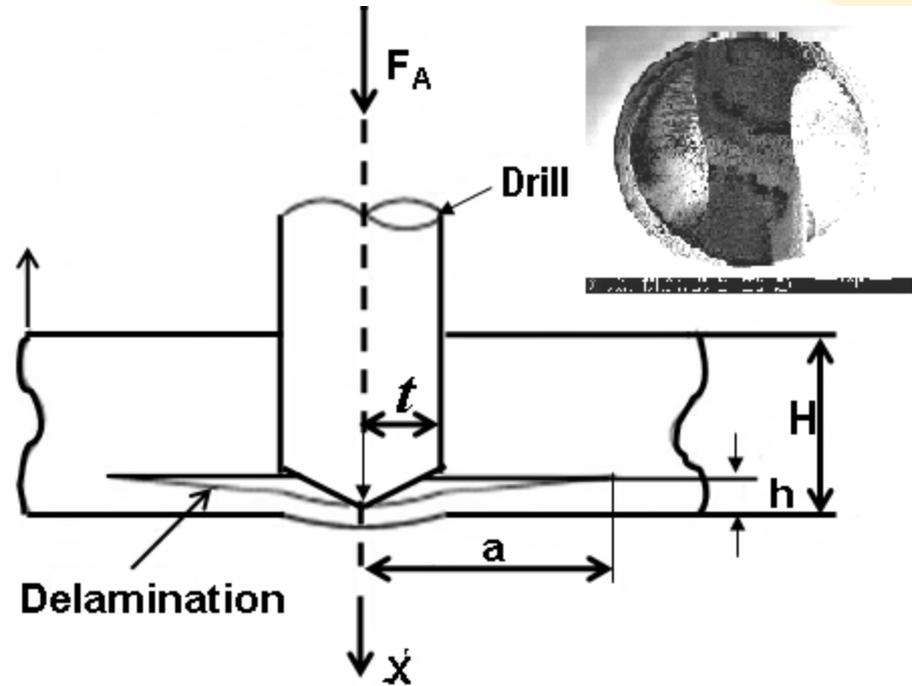
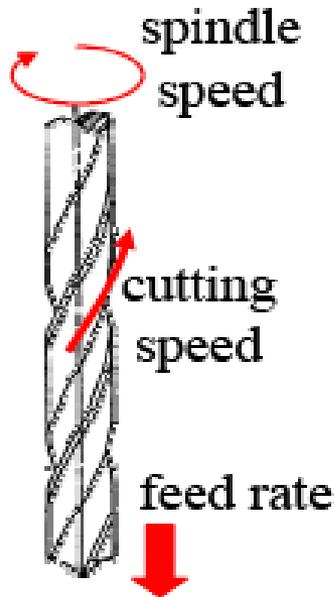


Hahn et al., *J. Polym. Sci., Part B: Polym. Phys.* Vol. 45, 3338 (2007)

Dispersion of the Tougheners in a Laminate Formulation



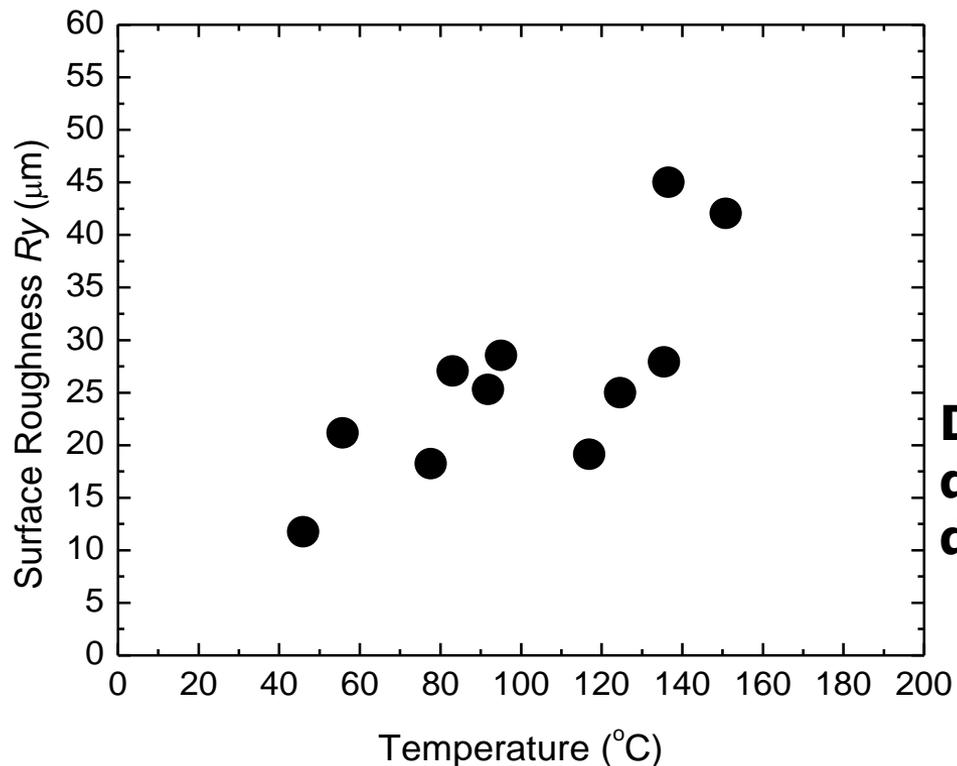
Typical Fabrication Parameters



Spindle speed: 110,000 rpm
 (0.3 mm diameter drill = 104 m/min)
 Feed rate: 70 in/min

$$F_A = \pi \sqrt{32G_{IC}M} = \pi \left[\frac{8G_{IC}Eh^3}{3(1-\nu^2)} \right]^{\frac{1}{2}}$$

Temperature Dependence of Surface Roughness



Drill-hole surface roughness deteriorates with increasing drill-bit temperature

Nakagawa et al., *Journal of Materials Processing Technology*, 191 (2007) 293 (data was digitized)

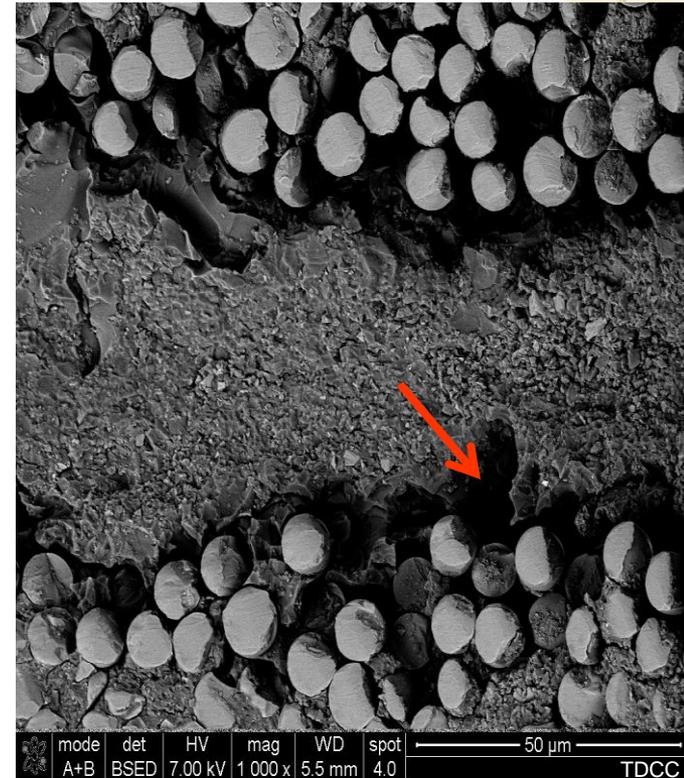
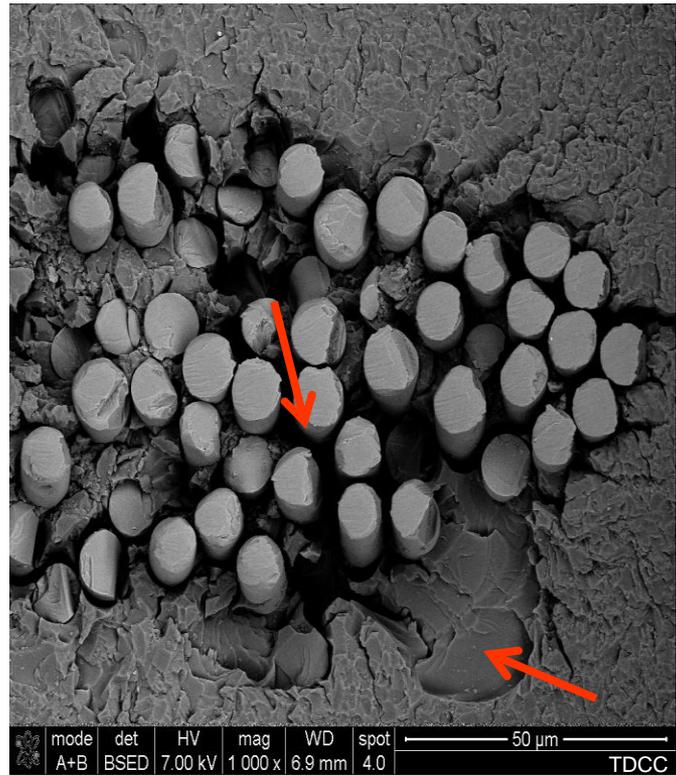
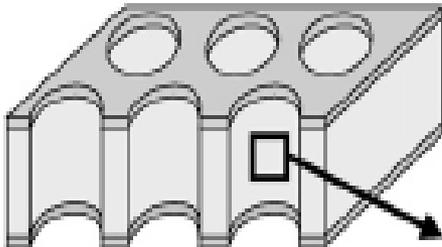
Target Thermomechanical Properties

Property	Target
Tg (°C)	175
Td (°C)	330
CTE(<Tg) ppm	60
CTE(>Tg) ppm	250
Moisture Uptake (%)	<0.5
Solder Pass (%)	100
T288 (min)	>15
Copper Peel (lb/in)	>7
UL94	V-0

Thermomechanical Properties

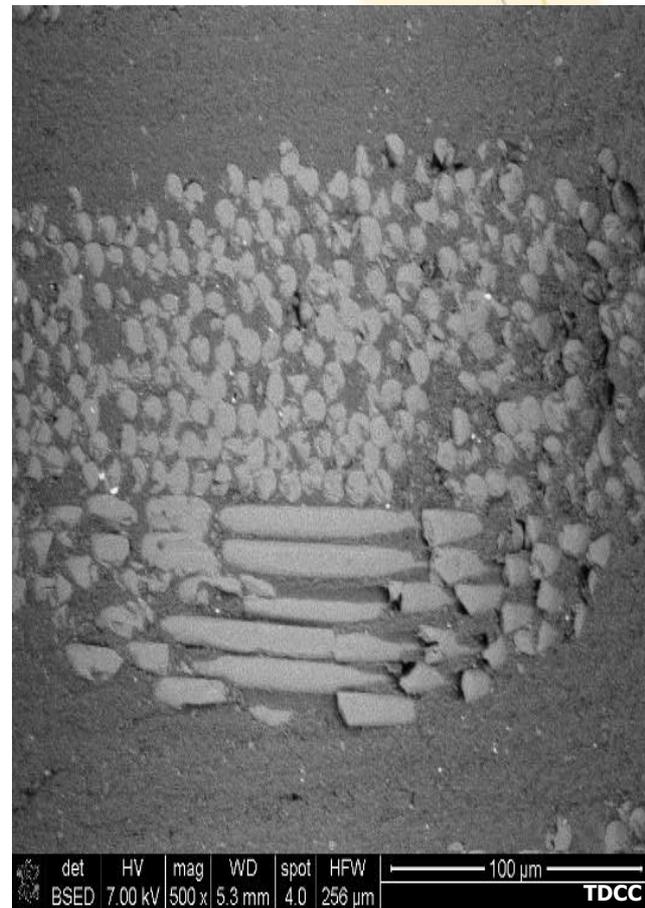
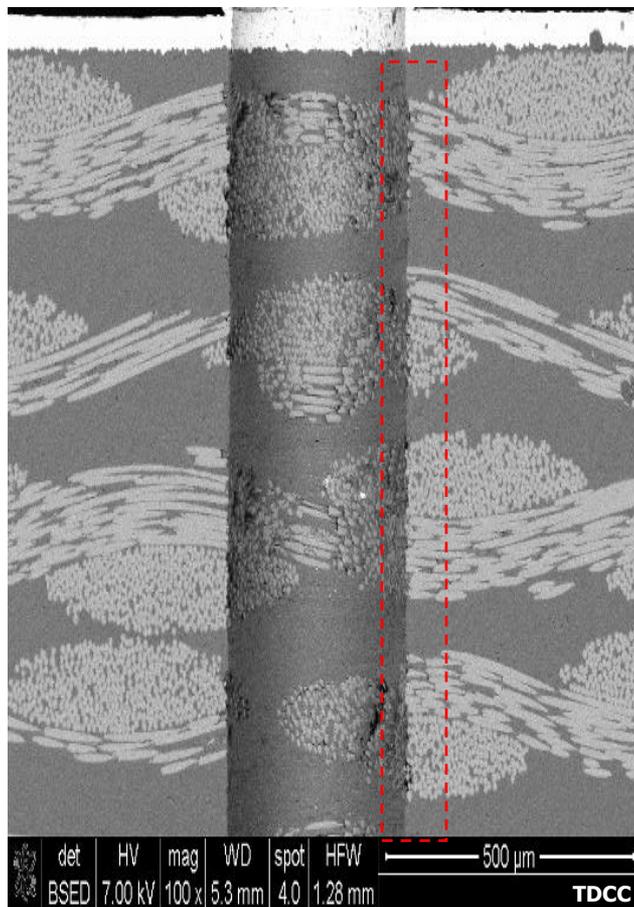
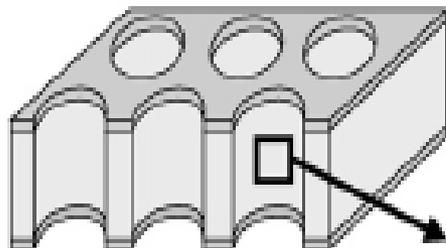
Parameter	Control	Sample 1	Sample 2
Toughener Loading Level (wt%)	0	3.75	7.5
Laminate Thickness (mm)	1.57-1.70	1.37-1.60	1.73
Tg3 (° C)	177	173	177
Td (5wt% loss) (° C)	363	365	361
Resin Content (%)	42.1	41	42.5
T288 (min)	30.2	26.2	41.5
CTE <Tg (ppm/° C)	60	35	50.1
CTE >Tg (ppm/° C)	260	228	203.6
Copper Peel (lb/in)	7.63	7.92	7.1
Moisture Uptake (%)	0.25	0.2	0.36
Solder Dip 550 F (% Pass)	100	100	100
UL 94 Rating	V-0	V-0	V-0

Drill Hole Surface Roughness – non-toughened formulation



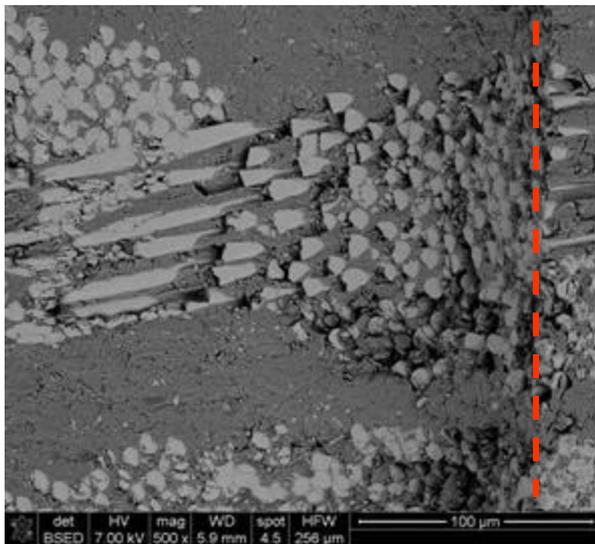
Significant microcracking, debonding observed for a non-toughened high T_g laminate

Drill-hole Surface Roughness of the Toughened Laminate

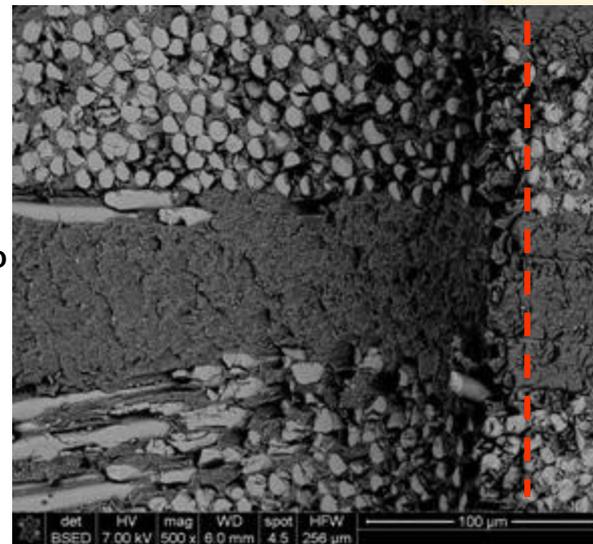


Drill-hole surface quality improves significantly for a toughened high Tg laminate

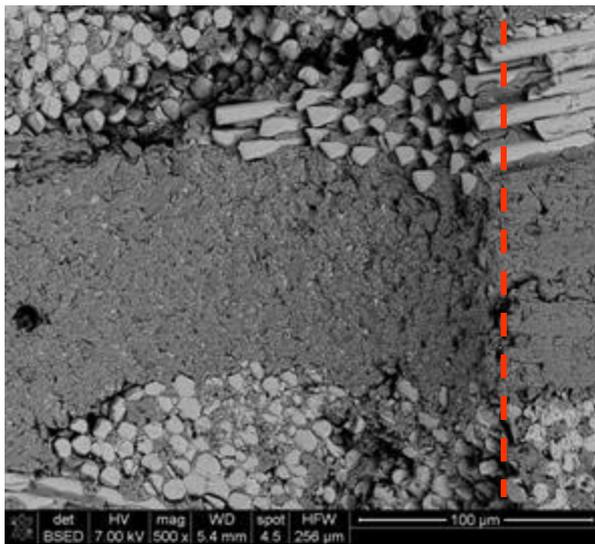
Drill-hole Surface Roughness Dependence of Loading Level



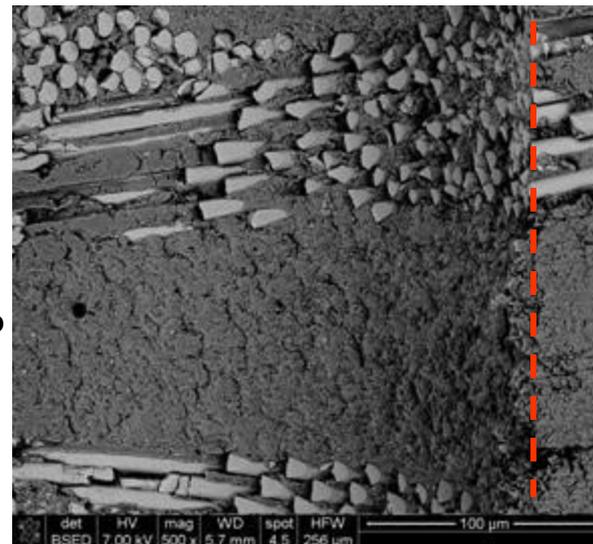
1st 0%



1st 3.75%

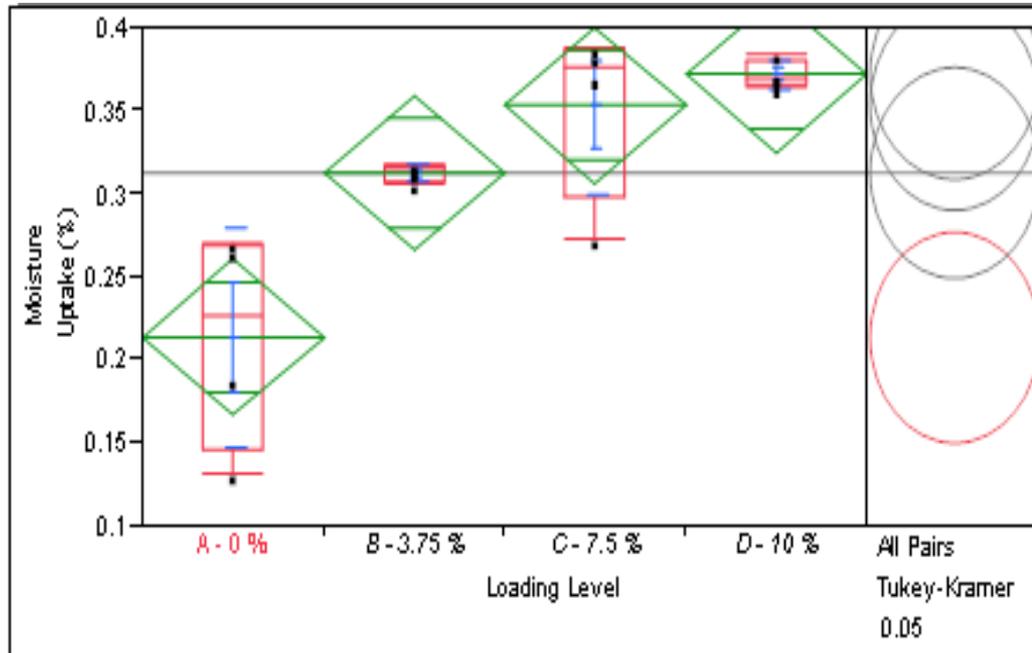


1st 7.5%



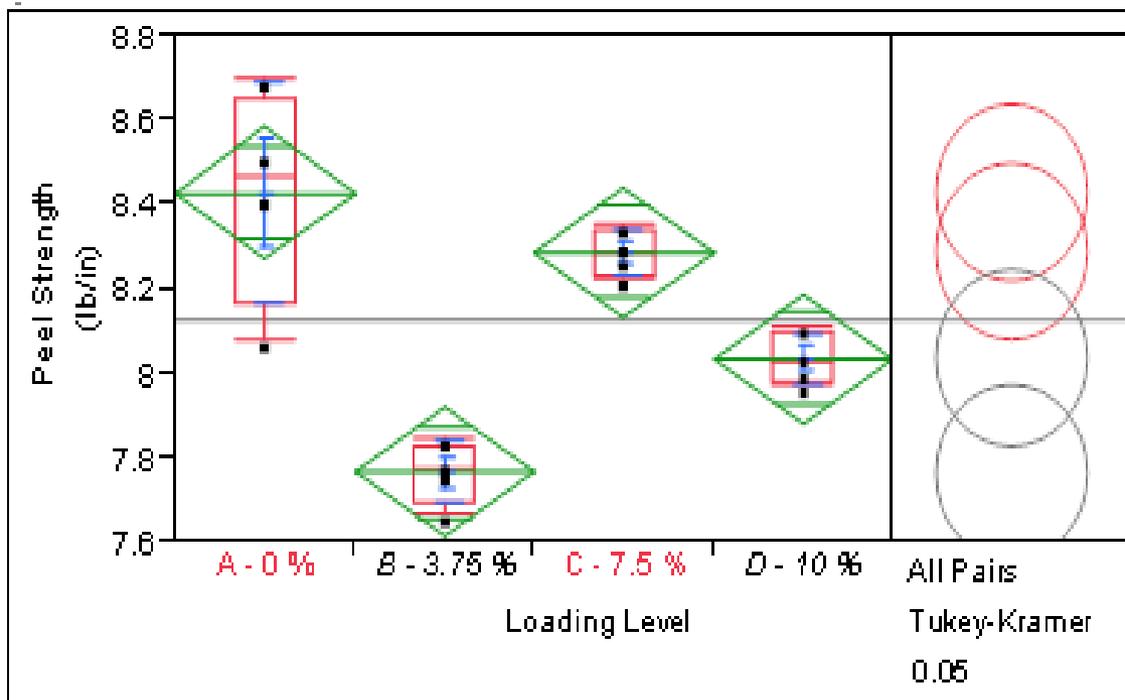
1st 10%

Loading Level Dependence of Moisture Uptake



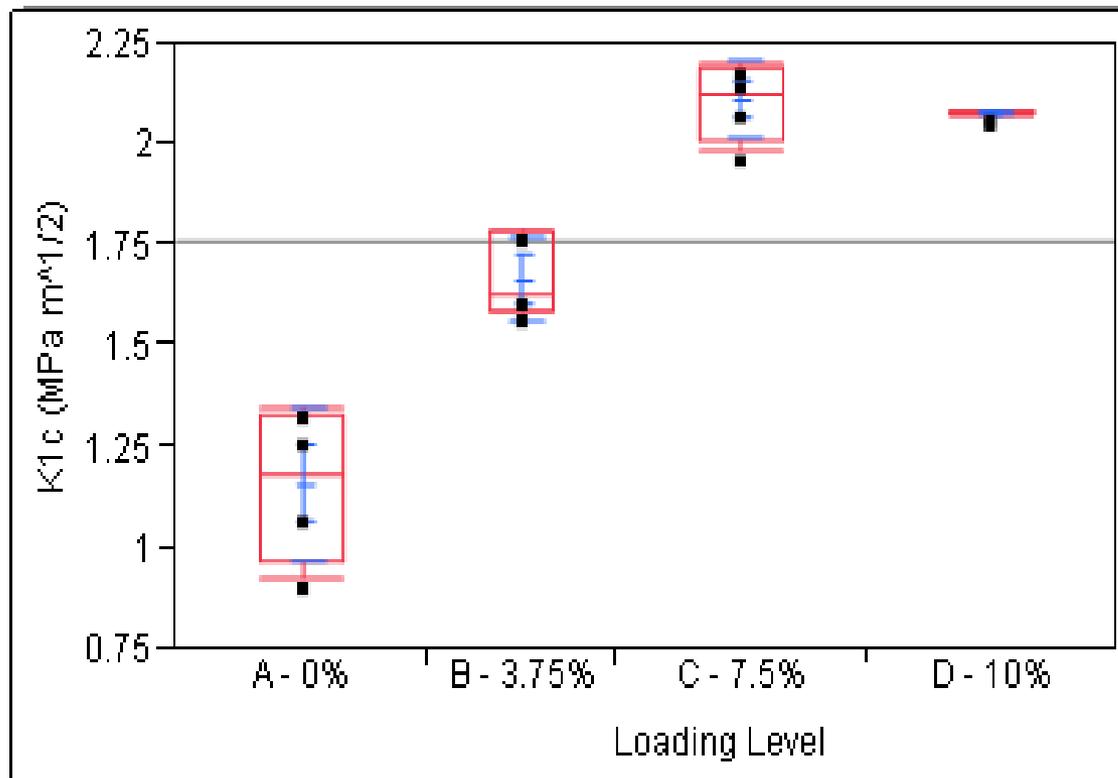
Moisture uptake exhibits weak loading level dependence above 3.75 wt%

Loading Level Dependence of Copper Peel



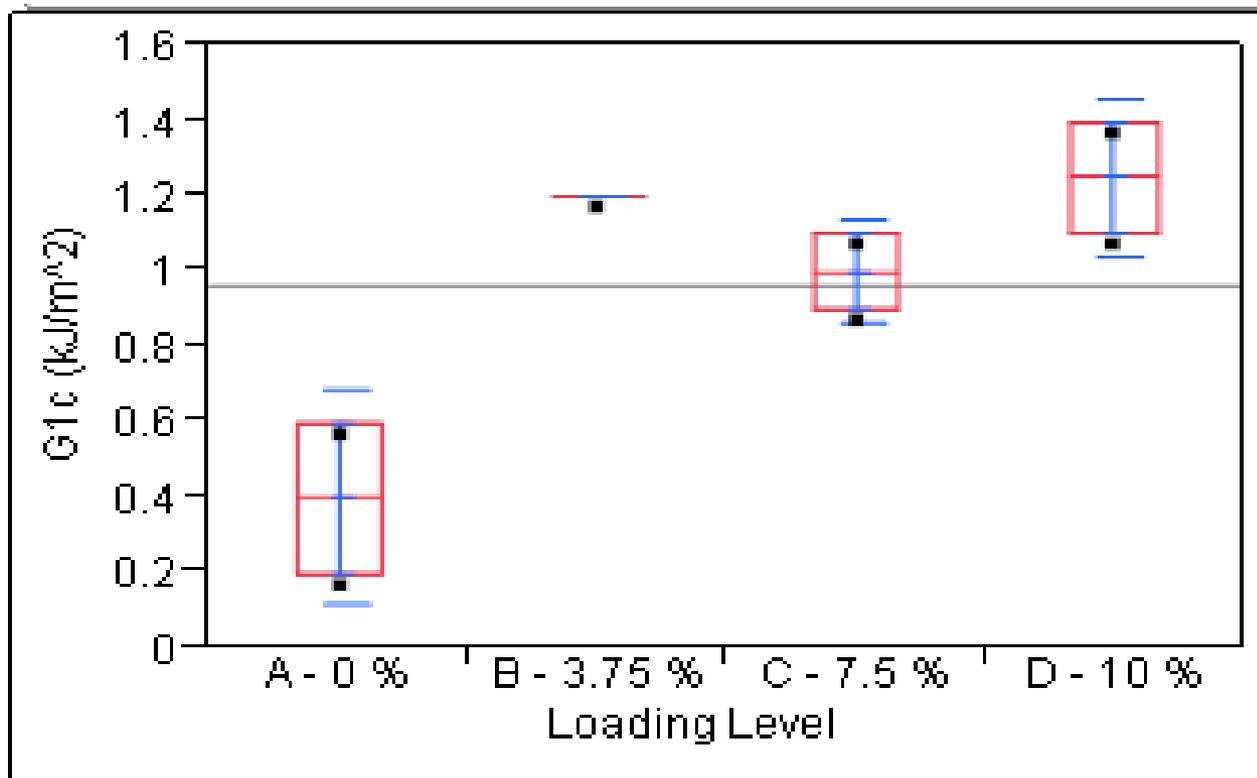
A decrease in copper peel with toughener loading is observable

Loading Level Dependence of Fracture Toughness



Above 3.75 wt% loading, no significant change in fracture toughness

Loading Level Dependence of Interlaminar Fracture Toughness



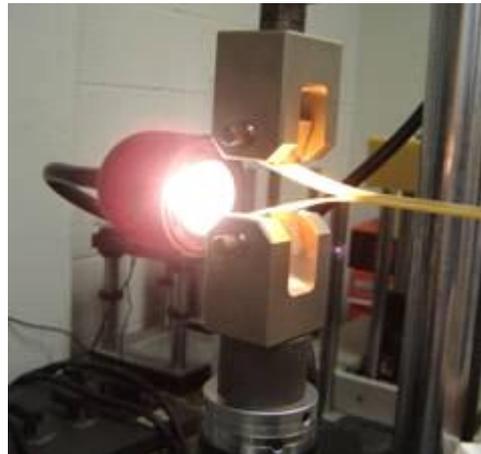
Interlaminar fracture toughness plateaus at 3.75 wt% loading

Cohesive vs. Adhesive Failure



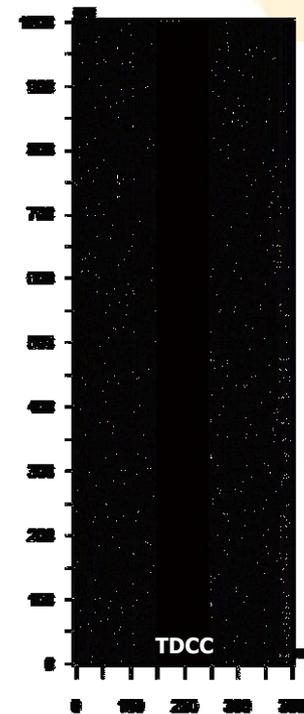
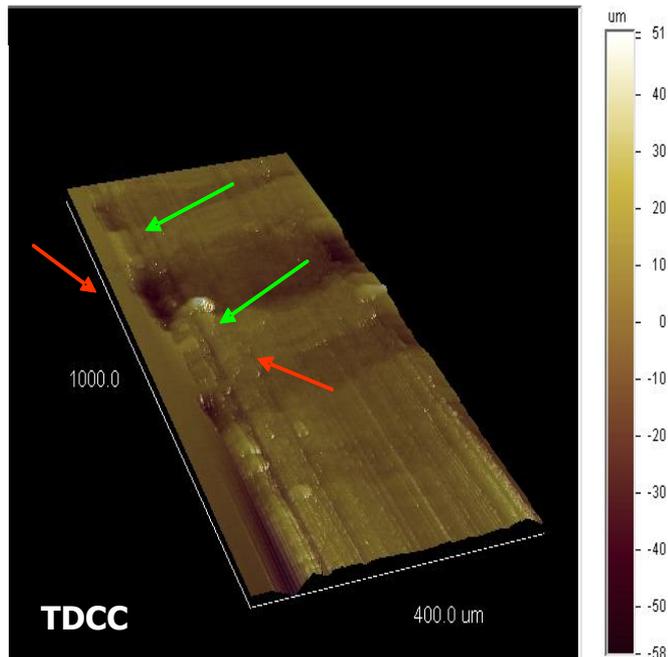
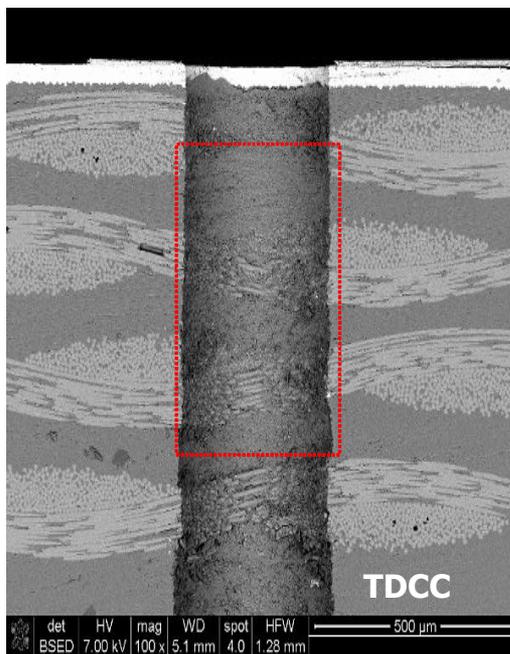
0 %

7.5 %



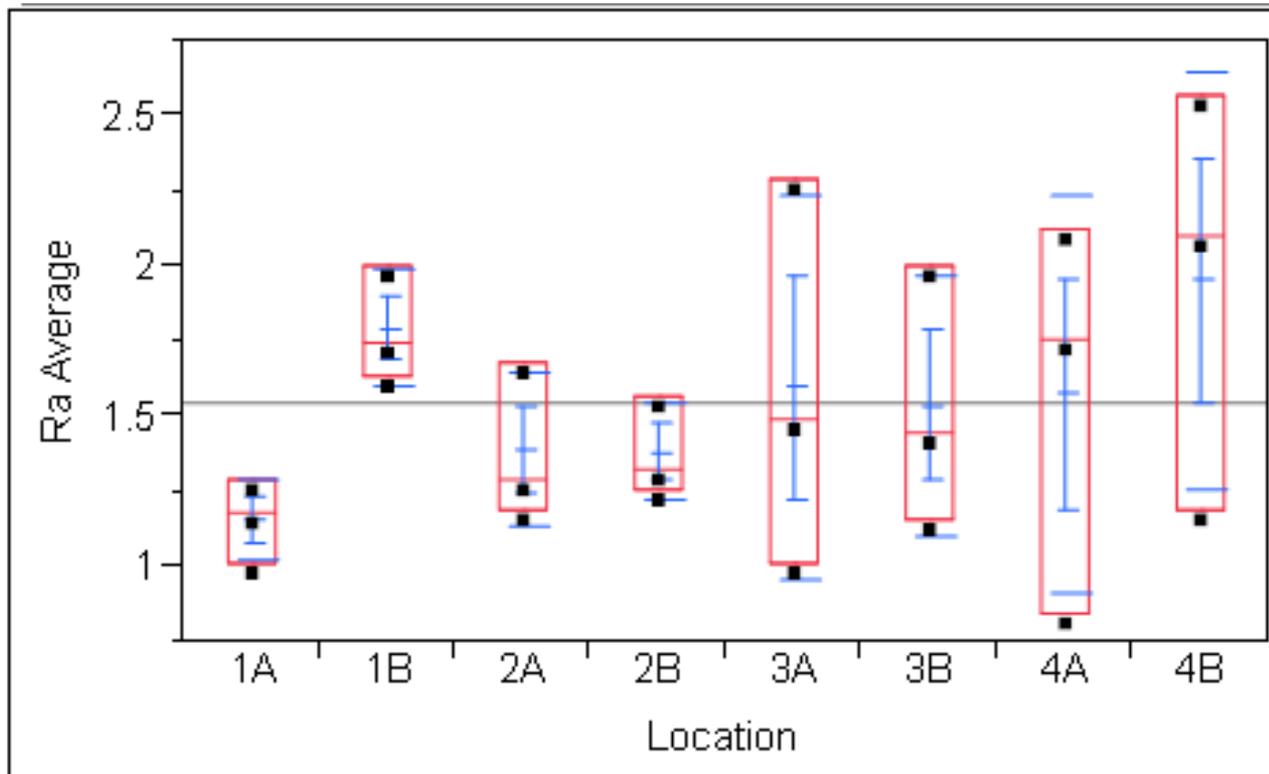
Transition – cohesive to adhesive failure observed with increasing toughener loading

Evaluation of Drill Hole Surface Roughness



$$S_a = \frac{1}{MN} \sum_{k=0}^{M-1} \sum_{l=0}^{N-1} |z(x_k, y_l) - \mu|$$

Drill-hole Surface Roughness Dependence of the Loading Level



Test Vehicle: A = beginning, B = end

1 = Control. 2, 3, and 4 = 3.75, 7.5 and 10 wt% toughener loading

Impact of Toughening on Thermomechanical Properties

Property	Impact
Tg via DSC	↔
5 % Decomposition Temperature	↔
Burn Times	↑
Moisture Uptake	↑
Copper Peel Adhesion	↔
PCT followed by 288 ° C Solder Dip	↔
K1c Values	↑
G1c Values	↑
Hole Wall Appearance (SEM)	↔
Hole Roughness (toughener loading)	↔
Hole Roughness Difference (beg to end)	↓
Fiber Pull Out	↔

Summary

- A high thermal stability resin formulation has been developed
- Brittle failure is observed subsequent to drilling of the non-toughened resin
- A toughening package has been developed that improves toughness without decreasing thermal properties
- Drill-hole surface quality significantly improves with the administration of toughener to the epoxy formulation
- Drill-hole surface quality deteriorates with increasing temperature of the drill-bit
- A cohesive to adhesive failure mechanism in the laminate is observed subsequent to toughener addition

Toughener Offering

- Toughening package is currently available