The Effect of the Incorporation of Tougheners on the Drillability of Epoxy-based Electrical Laminates

Lameck Banda, James Godschalx, Robert Hearn, Michael Mullins
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Abstract

The transition to lead-free solders has presented significant challenges for the electronics industry. One of the challenges is that typical lead-free soldering temperatures are much higher than those of tin-lead alloys. To maintain the reliability of printed circuit boards (PCBs) subsequent to higher assembly and rework requires new chemistries are required that give rise to materials with high glass transition (T_g) and high decomposition temperatures (Td). Increasing the crosslink density of a resin formulation is a common method used to achieve high T_g. Therefore, higher functionality resins and hardeners are being more commonly used. However, materials with high crosslink densities are also brittle. During the fabrication of PCBs holes are 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. Toughening agents are being incorporated into the resin formulations to improve drillability.

This work reports results from the study of incorporating toughening agents into resin formulations and their effect on the toughness and drillability of electrical laminates. This work also reports on evaluation protocols that account for the high temperatures and strain rates that the laminates are subjected to during the drilling process. The objective of the work is to serve as a starting point in creating a toolbox that will help correlate the thermomechanical properties of the resin formulations to the drillability performance of the corresponding PCBs. These correlations can 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

The global electronics industry is moving towards lead-free solders[1,2] for the fabrication of epoxy-based electronic devices. This requires high glass transition (T_g) and high decomposition temperature (Td) laminate materials. Traditionally, DiCy has been used as the hardener in the formulation of epoxy thermosets for electronics. However, given the new requirements, the T_g and Td for these cured structures is generally too low. To increase T_g and T_d, a higher crosslink density epoxy system can be employed. This is easily obtained by using phenolic cured systems.

Phenolic cured resins, while providing the needed high T_g and high T_d, are brittle due to the high crosslink density. This lack of toughness causes defects stemming from the drilling of holes. In the fabrication of electronic devices such as printed circuit boards or interconnects, holes are drilled into the copper-clad multi-ply boards and later the drilled holes are plated with copper. The drilling of brittle laminates results in high drill bit wear and breakage. It further leads to the formation of cracks in the boards. The formation of cracks is a serious concern for manufacturers because the cracks are initiation sites for "in process" and "in service" failures. During the board processing, the cracks will wick process chemicals (for example, etchants) into the board which after heat exposure will destroy the resin matrix leading to "resin recession". Further, cracks provide an easy pathway for the electro-migration of copper under "service" conditions of high humidity, high bias voltage, high moisture content, surface and resin ionic impurities, glass to resin bond weakness, and exposure to high assembly temperatures. The growth of copper filaments into the cracks is known as conductive anodic filament (CAF). The drilling process is a very expensive step in the device fabrication process and thus the drilling parameters are optimized to obtain high quality holes and to minimize drill bit wear. Engineering process changes have not been successful in reducing drilling defects without significantly influencing the economics. To mitigate the effects of brittleness, toughening additives are typically employed as they are more cost effective than process engineering solutions.

The fabrication of electronic devices is further complicated by the fact that the drilling process is performed at very high cutting speeds. The high cutting speeds induce high temperature build-up in the drill hole as shown in Figure 1. As seen from the Figure, the laminate reaches temperatures that are in the vicinity of the glass transition. This temperature rise is significant because it negatively affects drill-hole quality as shown in Figure 2[3].

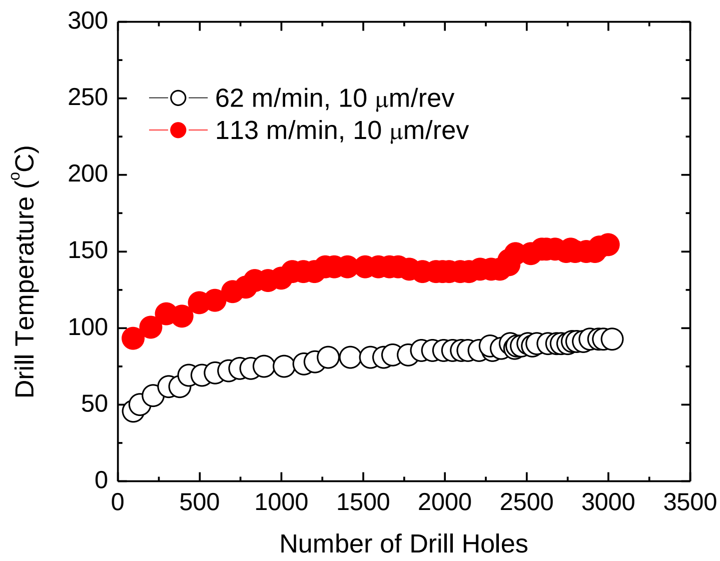


Figure 1. Temperature build up during fabrication of through holes for a glass fiber reinforced plastic[3] (data was digitized)

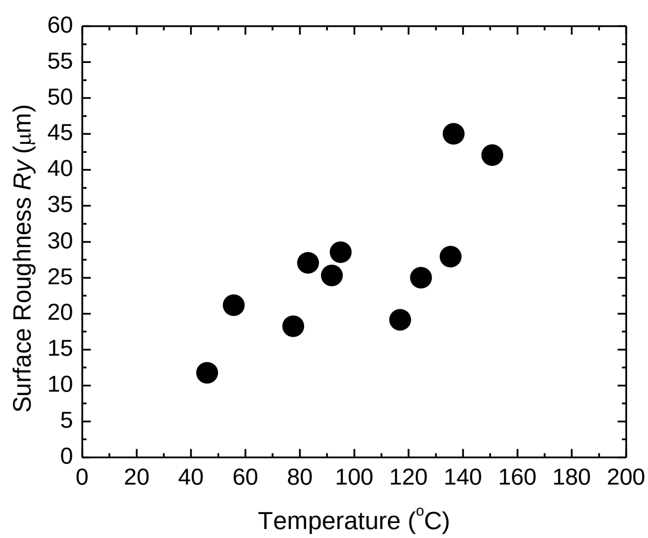


Figure 2. Temperature dependence of the surface roughness of drill-holes[3] (data was digitized)

A comprehensive evaluation of the thermomechanical properties and drill-hole surface quality of a select number of epoxy formulations with and without added toughening agents was performed. Results are compared with those of the non-toughened Control formulation. Observations from the work reported here using profilometry show that the non-toughened Control laminate exhibits a rougher drill-hole surface than the toughened laminate. It is worth mentioning here that when trying to quantify the microcracking and delamination, profilometry is insensitive to these specific surface defects as observed in the formulations evaluated here (the stylus of the profiler used in this work had a tip with a 2.5 □ m radius). Apparently, profilometry as currently practiced can not quantify or even detect the existence of the delamination or microcracking originating at the drill-hole surface. This is very important because in considering the relative importance of drill hole surface defects, delamination is of greatest importance compared to other defects such as surface roughness. Moreover, presently an industry wide accepted quantitative evaluation methodology for drill-hole defects does not exist. Currently, we are working on a drill-hole defect quantification methodology and results will be shared later.

2.0 Experimental

2.1 Materials

Laminate boards were prepared from B-staged prepregs. 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 TA1 toughener was predispersed 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 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 (2-methylimidazole) was added as needed to adjust the reactivity.

2.3 Fracture Toughness

High strain rate fracture toughness evaluations were performed using an MTS High Rate servo hydraulic frame. A 500 lb capacity load cell was used to measure the load deflection. The instrument is equipped with two 252 servo valves. The valves control an actuator that measures the displacement change. Custom pin loaded fixtures were used to mount the sample. The high strain rate tests were run at 230 in/min and the data were captured at a rate of 0.0002 sec/point. The output file was analyzed and maximum values were selected to calculate fracture toughness. Samples were fabricated using the compact tension geometry and measured in Mode I fracture where the fracture toughness (K_{1C}) is calculated using the relationship[4]:

$$K_{1C} = \frac{P * Y\left(\frac{a}{W}\right)}{B * W^{0.5}}$$

where *P* is the load, *Y* is a geometric factor depending on crack length (*a*), *W* is the width of the specimen, and *B* is the thickness of the specimen.

3.0 Results

As indicated in Figure 1, the drilling process is performed under very high strain rates. The high strain rates induce high drill-bit temperature build-up. The high temperature build-up in the drill-hole negatively affects drill-hole surface quality. In order to evaluate the fracture toughness of the laminates under conditions that mimic actual drill-hole fabrication conditions, in this work we evaluated fracture toughness at high strain rates. Figure 3 shows the critical stress intensity factors (K_{1C}) for the Control formulation that has now been toughened by three different but similar toughening agents. The strain rate used here is five orders of magnitude higher than the standard quasi static rate, but still 20 times slower than the drill-bit cutting speed. The results in Figure 3 show that the Control has lower fracture toughness than the toughened formulations. More importantly also, the fracture toughness at high strain rates is lower than that observed under quasi static strain test conditions. This result is important because it clearly illustrates the time-dependent behavior of these materials i.e., at high strain rates, the material behaves as if it were a more brittle structure. Additionally, this result is an indication that the efficiency of the toughening agent is negatively impacted at high strain rates. Particularly, one would want to know what the timescale for toughening particle cavitation is. If the timescale of particle cavitation is slower than the fracture rate, then the effectiveness of the toughening particle is negatively impacted. Results on these studies will be shared later. This result also implies that the actual material toughness under the cutting speed used in via fabrication is much lower than that exhibited under the quasi static evaluation conditions. This is important because currently there is no evaluation methodology that can correlate material toughness to drillability. Evaluation of fracture toughness at high strain rates may be a good starting point to achieving this correlation.

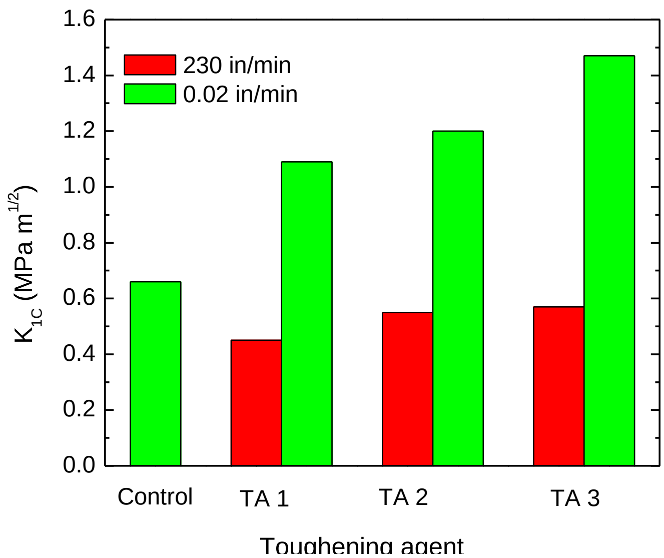
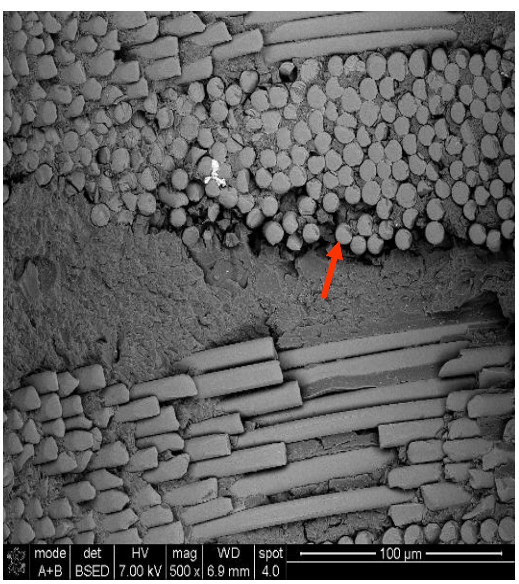


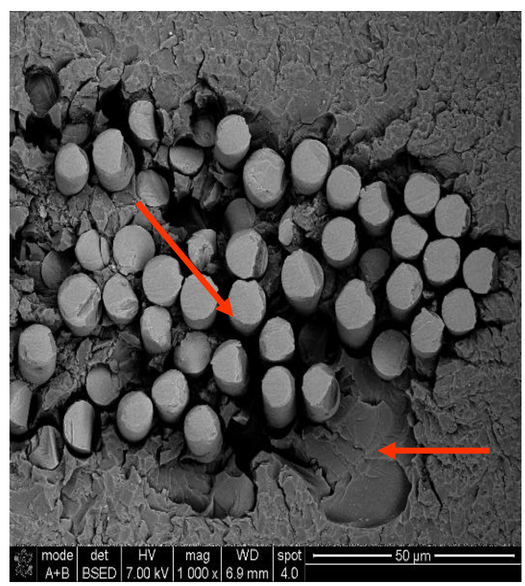
Figure 3. Critical stress intensity factor (K_{1C}) values for toughened formulations compared with the non-toughened formulation at different strain rates

The drillability of the non-toughened formulation is shown in the micrographs depicted by Figures 4(a, b). This system is used as a Control for the TA 1 toughened formulation shown later. Figure 4(a) shows the nature of debonding of the resin from the fiber where very clean fibers are indicative of perfect debonding. The higher magnification Figure 4(b) shows the failure in the resin/fiber interface very well. The Figure also shows loss of resin in this region in what looks like a brittle failure process. This is illustrated by the loss of resin extending further into the bulk resin region. Such failure is catastrophic because it will negatively affect the uniformity of copper plating and furthermore, such surface defects are potential initiation sources for microcracking subsequent to thermal cycling.

The drill hole surface roughness of the TA 1 toughened formulation is shown in Figures 5(a,b). The topography of the drill-hole surface looks very smooth. The higher magnification images, Figures 5b, show that the integrity of the fiber-matrix interface is preserved subsequent to drilling in this sample. There does not appear to be evidence of debonding. This is a complete contrast to the control sample shown in Figures 4 (a,b) where significant brittle failure was observed. These observations show that addition of TA 1 toughener improves drillability of the laminate board.

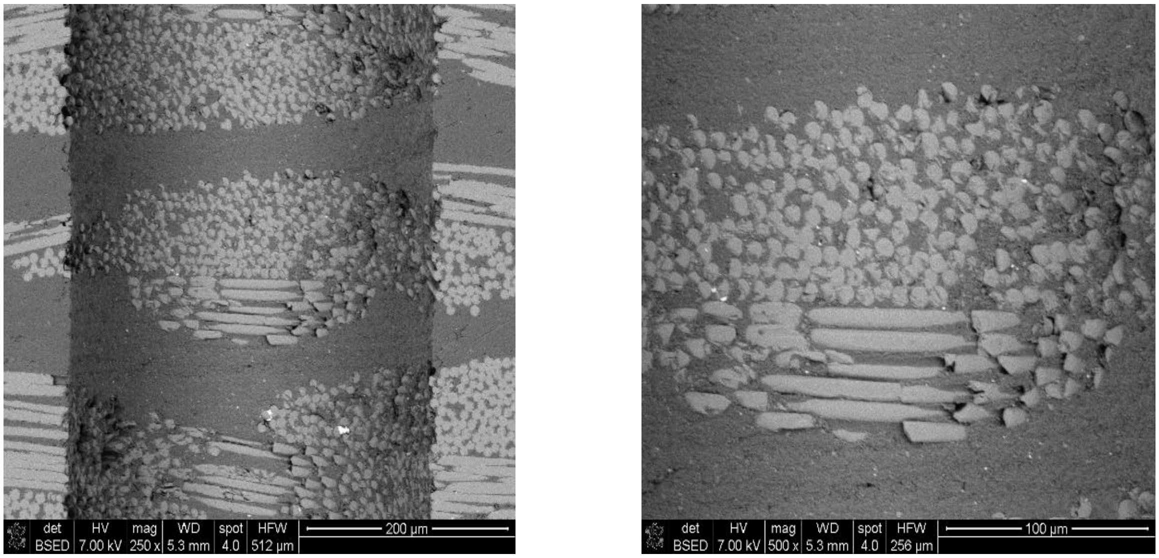


(a)



(b)

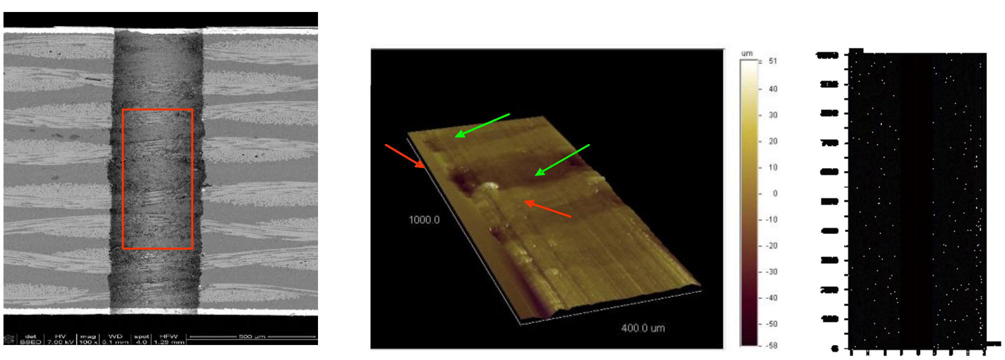
Figures 4(a,b). Drill-hole surface for a non-toughened laminate formulation showing fiber debonding and brittle failure



(a) (b)

Figures 5(a,b). Drill-hole surface of a laminate formulation toughened with TA 1. The base formulation is the same as the one shown in Figures 4(a,b).

The SEM micrographs of the drill-hole surface above present a visual and qualitative outlook of the surface roughness. In order to more quantitatively rank the drillability of different resin formulations, we needed a more quantitative methodology. This was attempted in this work by mapping the topography of the drill-hole surface by using profilometry. Figures 6 (a-c) shows the drill-hole surface profile of the sampled area of the drill-hole surface. The surface generated from the drill-hole trough shows areas that are depressed in darker shades (green arrows) and areas that are higher in lighter shades (red arrows) as shown in Figure 6(b). The depressed areas occur in the resin between glass fiber tows. The shoulder of the trough is also shown in the profile surface. The data from the shoulder should not be used to calculate surface roughness parameters. An area in the center of the trough is selected for the roughness analysis as shown in Figure 6(c).



(a) (b) (c)

Figures 6. Surface profile showing the topography of a drill-hole surface mapped by profilometry.

A comparison of the average surface roughness of the drill-holes for the formulation toughened with the toughening agent TA1 compared with the non-toughened formulation are shown in Figure 7. Results show that the toughened formulation has the difference in the average surface roughness between the beginning and the end of a drilling cycle for a 2500 drill-hole array for laminates toughened with different toughening agents.

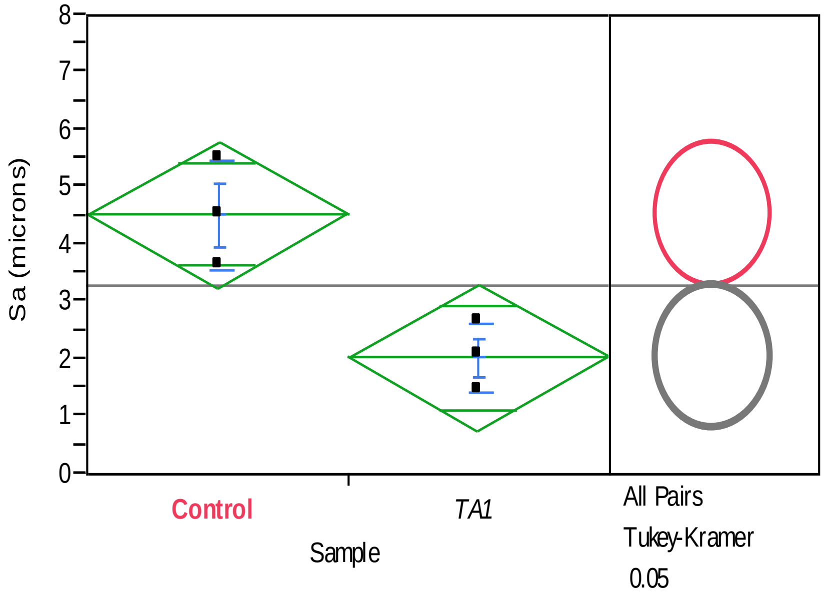


Figure 7. Average surface roughness for the formulation toughened with TA1 compared with the non-toughened formulation. statistically significant better surface roughness than the non-toughened formulation.

Additionally, as shown in Figure 8, profilometry is sensitive enough to pick up the trend in average surface roughness as a function of the number of holes drilled. Figure 8 shows

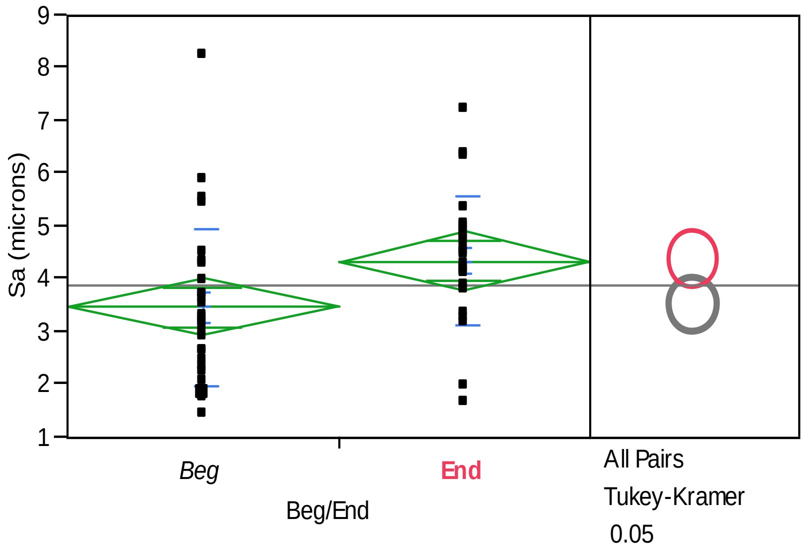


Figure 8. Difference in average surface roughness between the beginning and end of drilling for a 2500-hole grid

These results are consistent with the study shown in Figures 1 and 2 where with increasing number of drill-holes, drill-bit temperature increases and therefore, deteriorating drill-hole surface roughness.

4.0 Conclusions

An evaluation of the impact of a preformed toughening agent on the drillability of a phenolic cured electrical laminate was studied. Results show that whereas the non-toughened laminate exhibits brittle failure in the resin-fiber interface and in the bulk resin, a significant improvement is observed when a toughening agent is added.

The results reported here show that the actual fracture toughness of a toughened electrical laminate is diminished when evaluated at high strain rates for materials toughened with preformed tougheners. This is important because the drilling of holes in these boards is a high strain rate process. This result is also important because it serves as a first step in the development of a methodology to correlate material toughness to drillability.

5.0 References

1. Ehrler, S., *CircuiTree*, June 2005
2. Reid, P., *Printed Circuit Design and Fab*, 2008
3. Nakagawa et al., *Journal of Materials Processing Technology*, 191 (2007) 293
4. Sue, H.-J., Bertram, J.L., Garcia-Meitin, E.I., Wilchester, J.W., Walker, L.L., *Colloid and Polymer Sci.,* 272 (**1994**) 456

The Effect of the Incorporation of Toughness on the Drillability of Epoxy-based Electrical Laminates

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Motivation

- Advent of legislation requiring lead-free solders for printed circuit boards

➢ New phenolic cure chemistry being used in electrical laminates has allowed for higher decomposition temperature at the cost of brittleness and reduced adhesion to copper (which is mostly caused by lack of toughness).

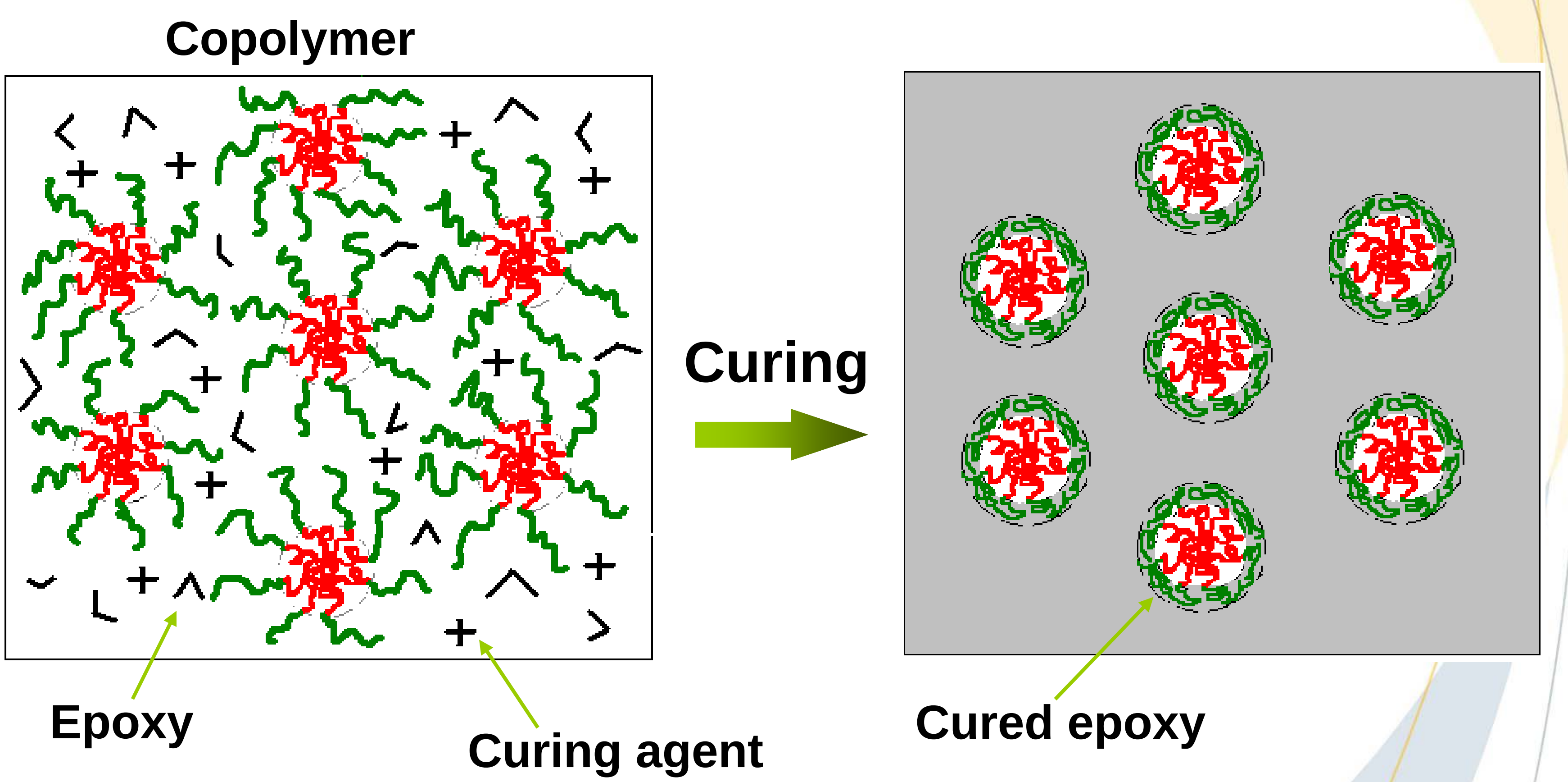
- Phenolic-cured laminates are brittle and cause drill bit wear and breakage. In addition, the irregular hole-surfaces reduce the reliability of plated-through-holes.

➢ A toughening agent would be of benefit to new products.

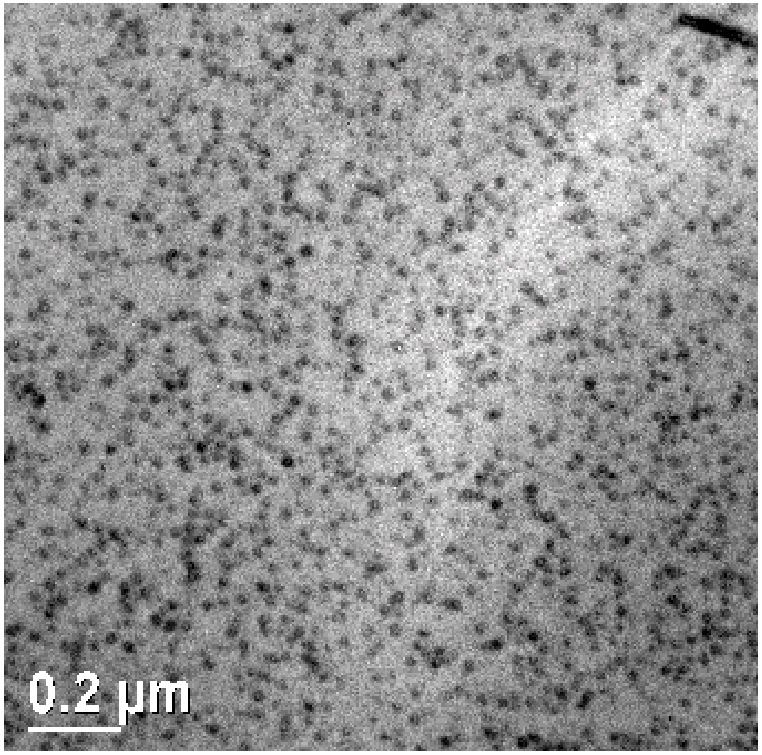
Outline

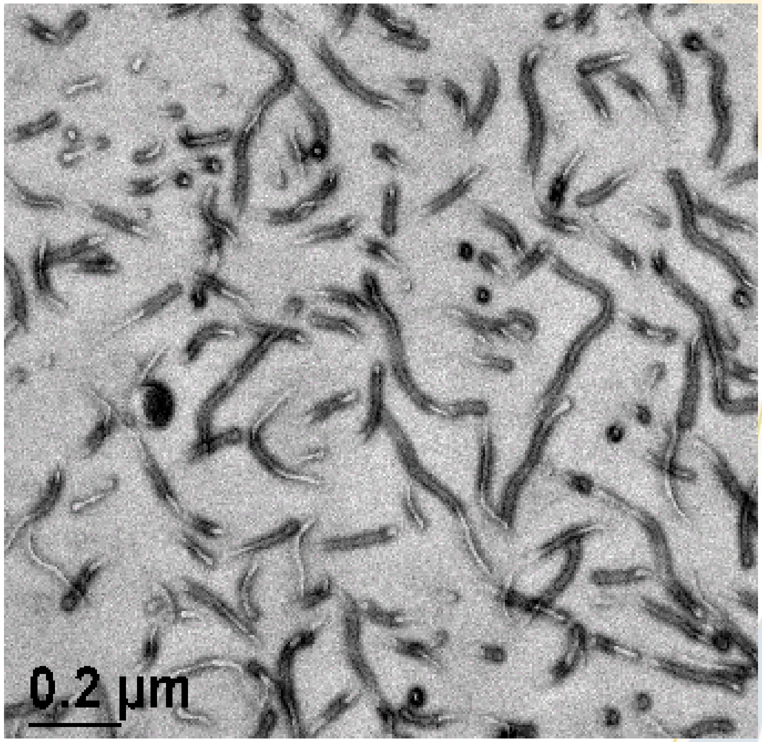
- Thermomechanical properties
- Drill hole surface roughness (Qualitative)
- Drill hole surface roughness (Quantitative)
- Conclusions

Background - FORTEGRA™



Self-assembled Morphologies

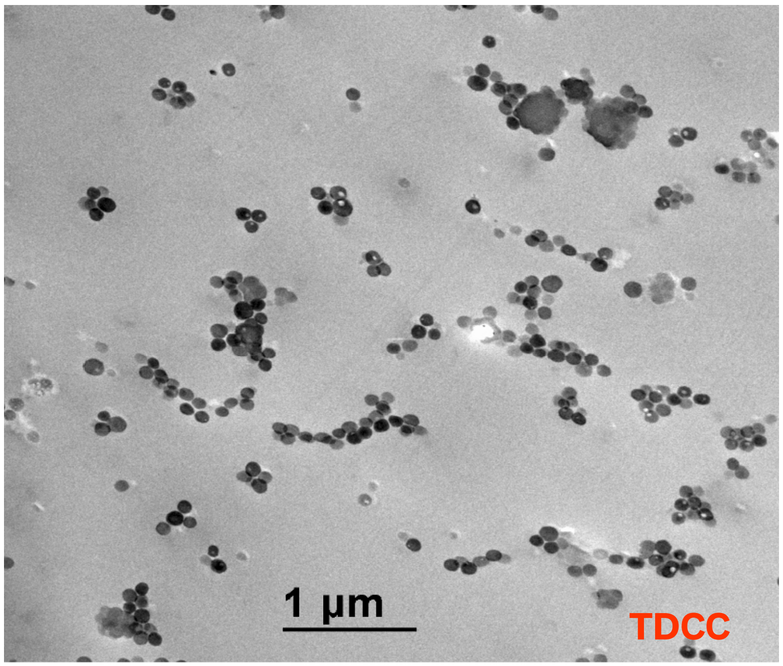




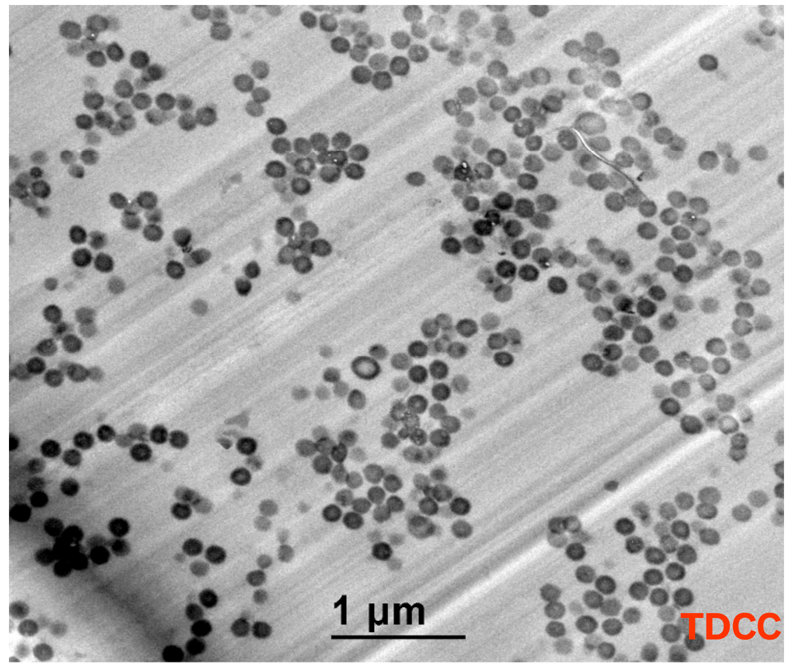
Hahn et al., *J. Polym. Sci., Part B: Polym. Phys*. Vol. 45, 3338 (**2007**)

Dispersion of the Tougheners in a Laminate Formulation

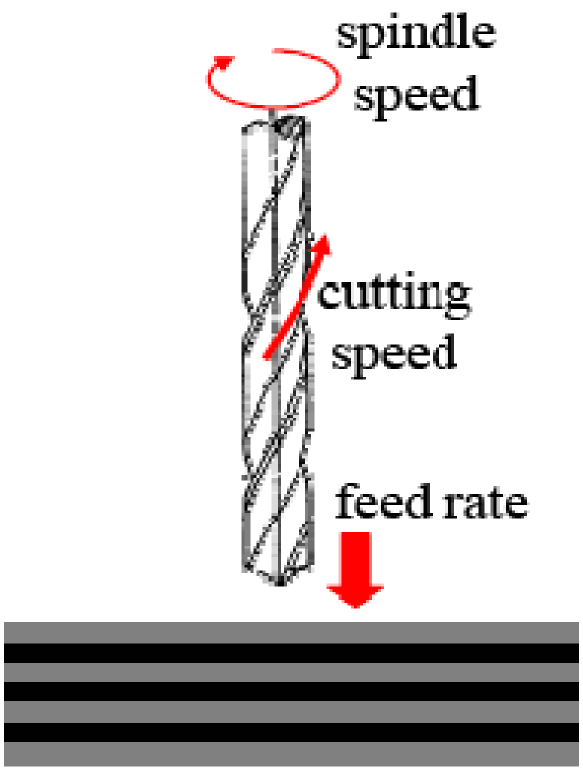
TA 1

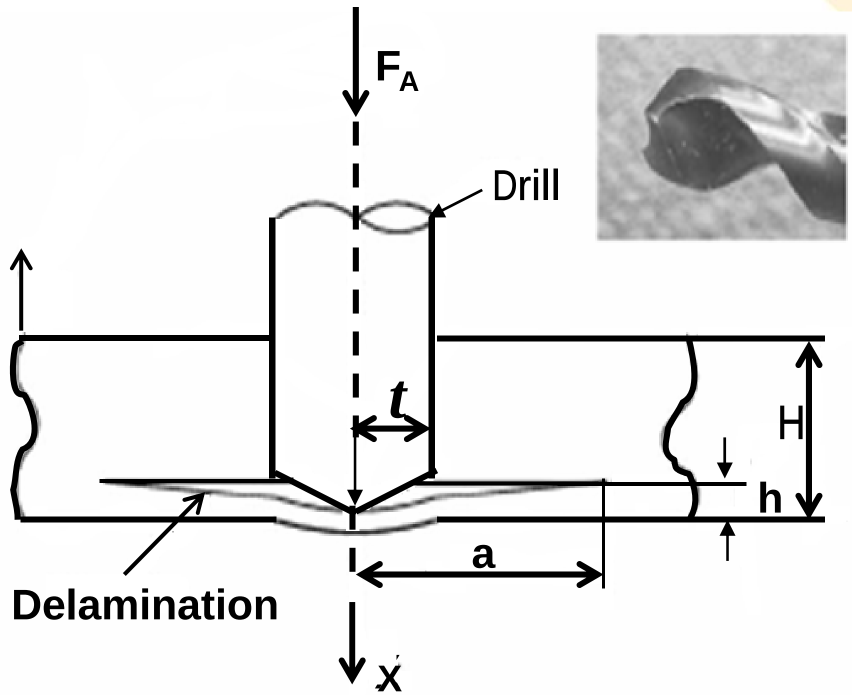


TA 2



Typical Fabrication Parameters



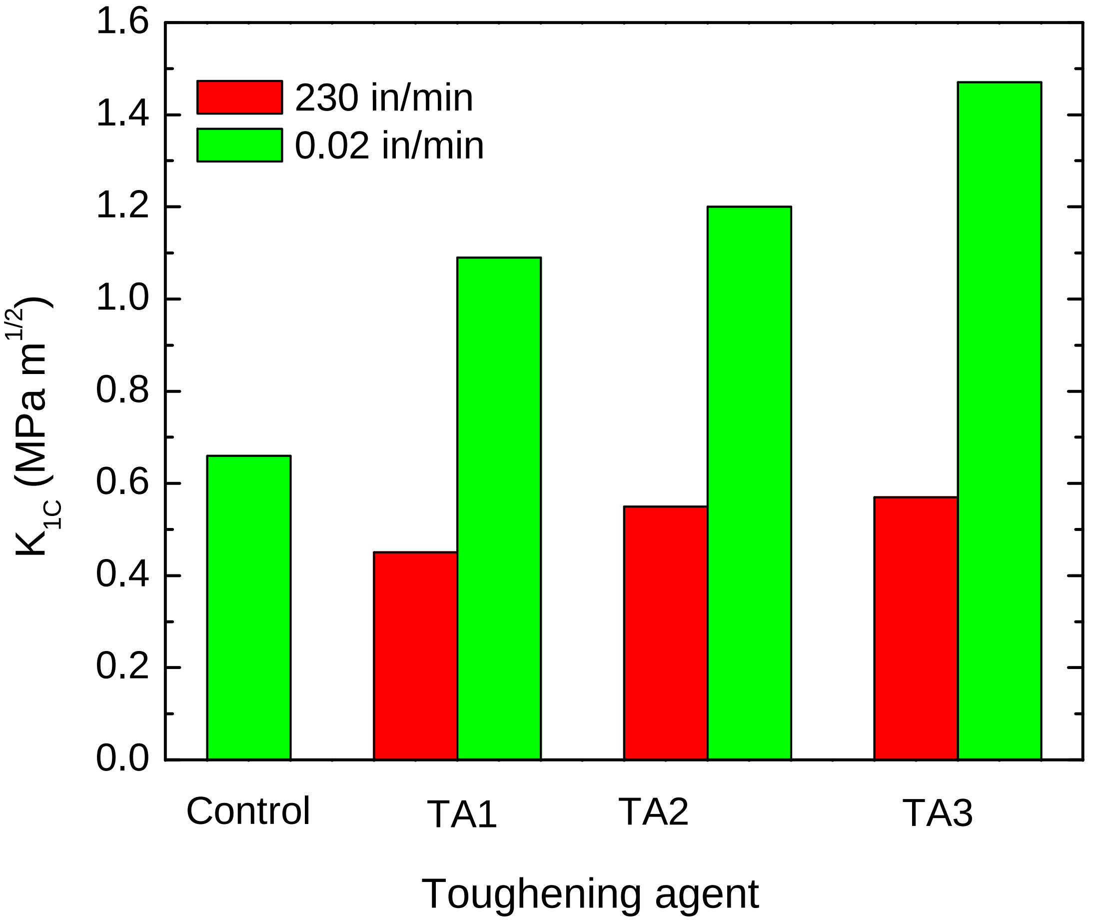


Spindle speed: 110,000 rpm
(0.3 mm diameter drill = 104 m/min)
Feed rate: 70 in/min

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

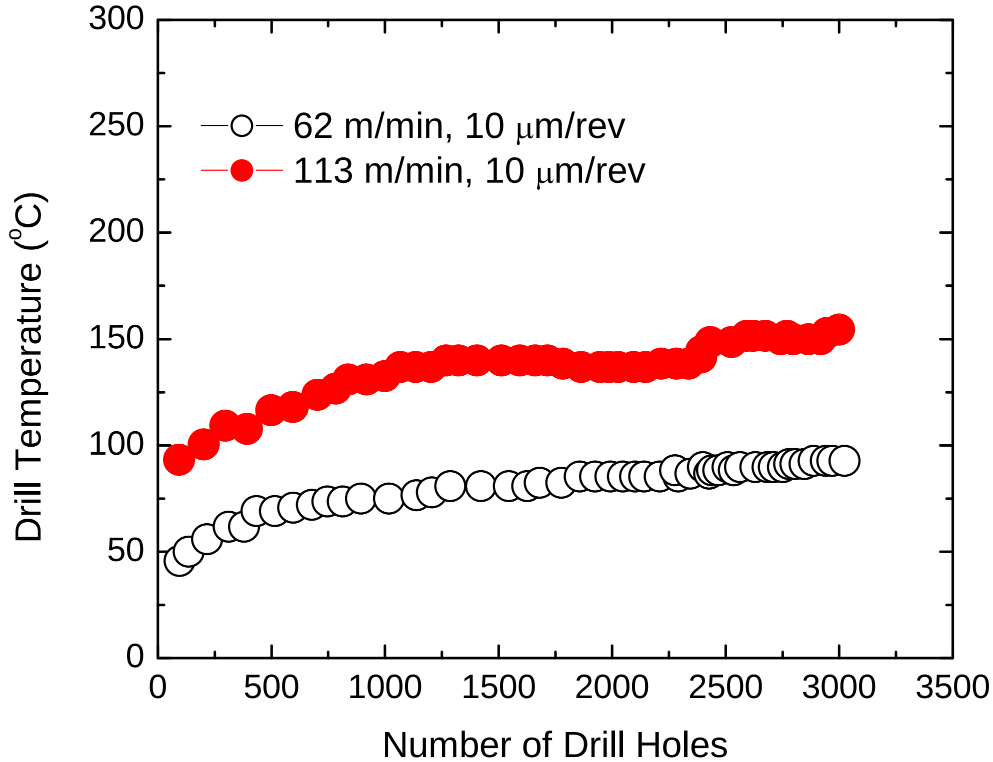
Hocheng et al., *J. Eng. Ind.,* 112 (**1995**) 236

High Strain Rate Fracture



$$G_{1c} = \frac{K_{1c}^{\;2}}{E}\left(1-\nu^{2}\right)$$

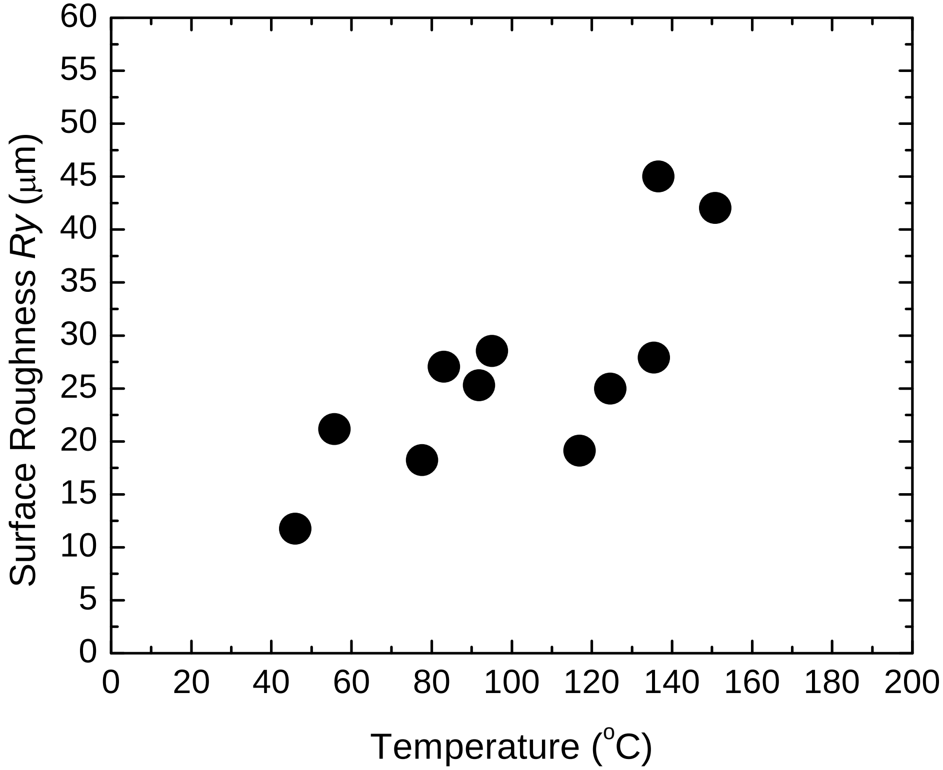
Temperature Build up During Fabrication of Through Holes for a GFRP



Drill-bit temperature is significantly impacted by the cutting speed

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

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)

Thermomechanical Properties of Different Formulations

Evaluation of Drill Hole Surface Roughness

Non-Lead Free Application – Dicyanamide hardener

1. High Tg brominated epoxy resin

Lead Free Application-Phenolic Hardener/18 % bromine

2. Bis A Epoxy Novolac

3. Phenolic Novolac Epoxy/Toughning Agent (TA2)

4. Phenolic Novolac Epoxy/Toughning Agent (TA1)

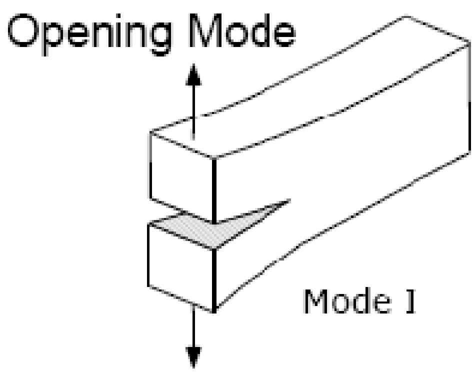
5. Phenolic Novolac Epoxy

Resin	Tg	Td (5% loss)	Moisture Uptake (%)
	°C		
1	179	296	0.42
2	200	363	0.27
3	168	357	0.22
4	177	361	0.35
5	180	365	0.25

TA1-toughened resin exhibits high Tg and Td

Thermomechanical Properties of Different Formulations

Resin	G1C	Copper Peel
	(kJ/m2)	(lb/in)
1	0.63	10.32
2	0.14	6.08
3	0.43	6.49
4	0.63	7.1
5	0.43	7.3



Interlaminar fracture toughness (G_{1C}) geometry

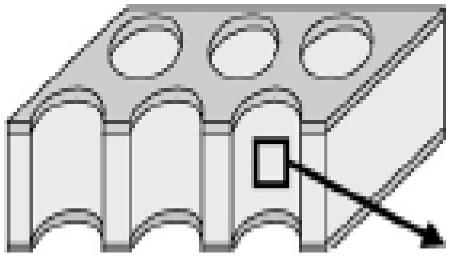
TA1 (#4) - toughened resin exhibits better interlaminar fracture toughness and copper peel strength

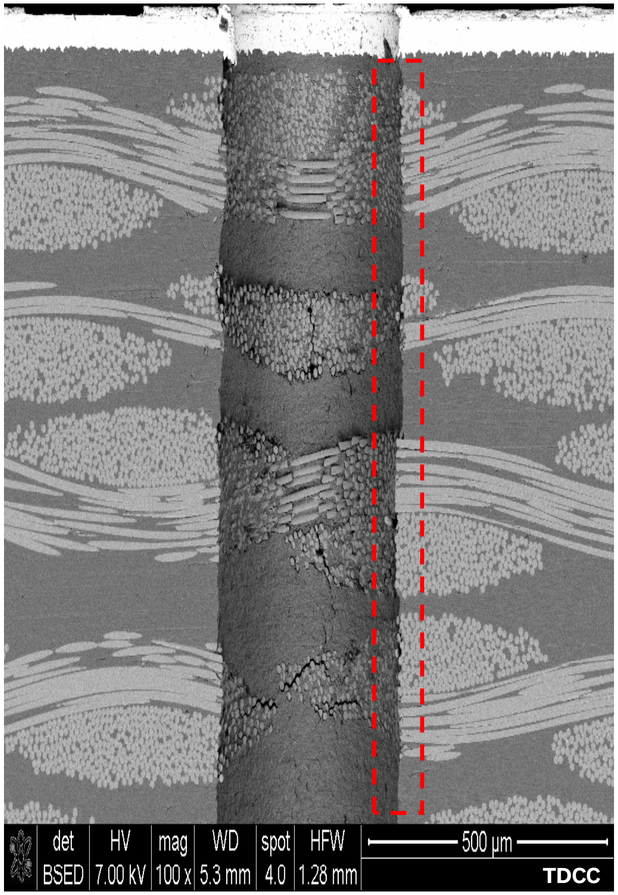
Thermomechanical Properties of the Formulations

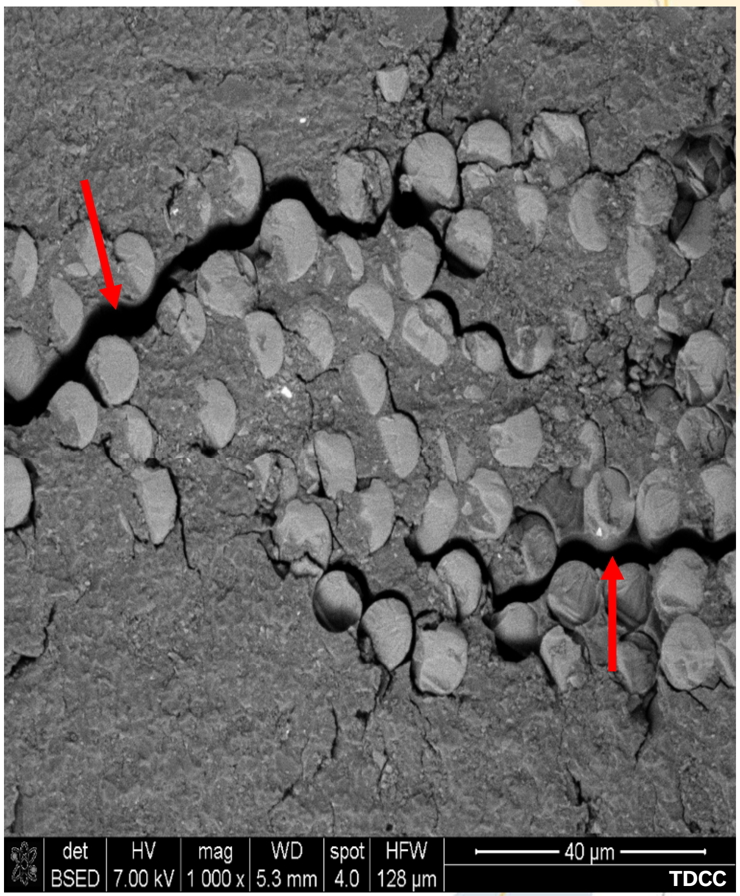
Resin	CTE < Tg	CTE > Tg	T288
	(ppm)	(ppm)	min
1	62	300	0.2
2	47	184	>30
3	64	274	23
4	50	204	42
5	51	230	43

The TA1-toughened resin exhibits good CTE and T288

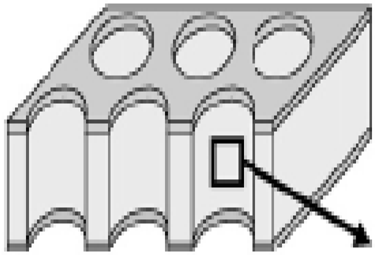
Drill Hole Surface Roughness – non-toughened (formulation # 2)

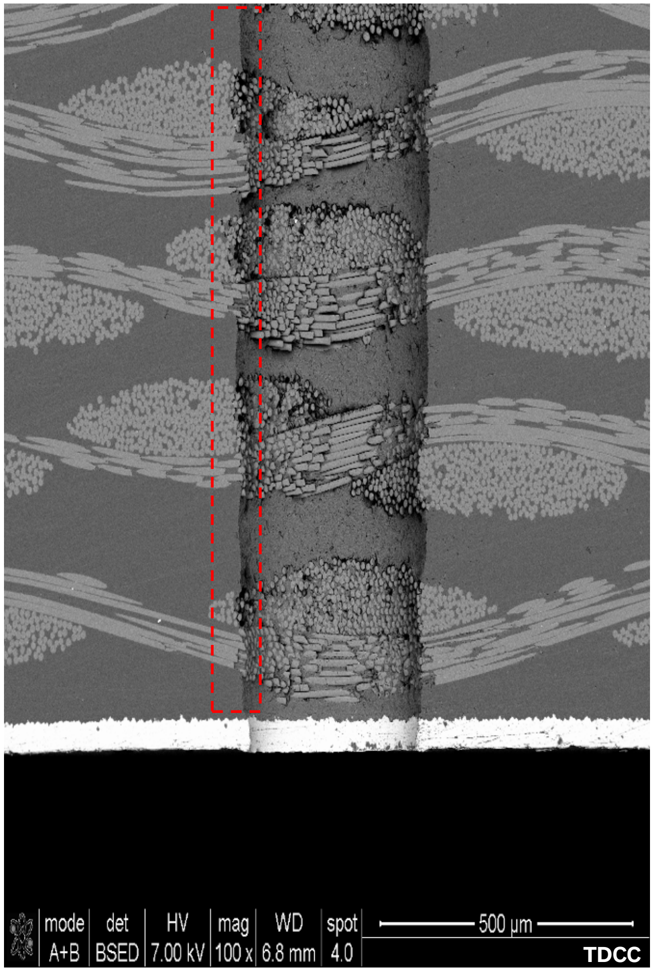


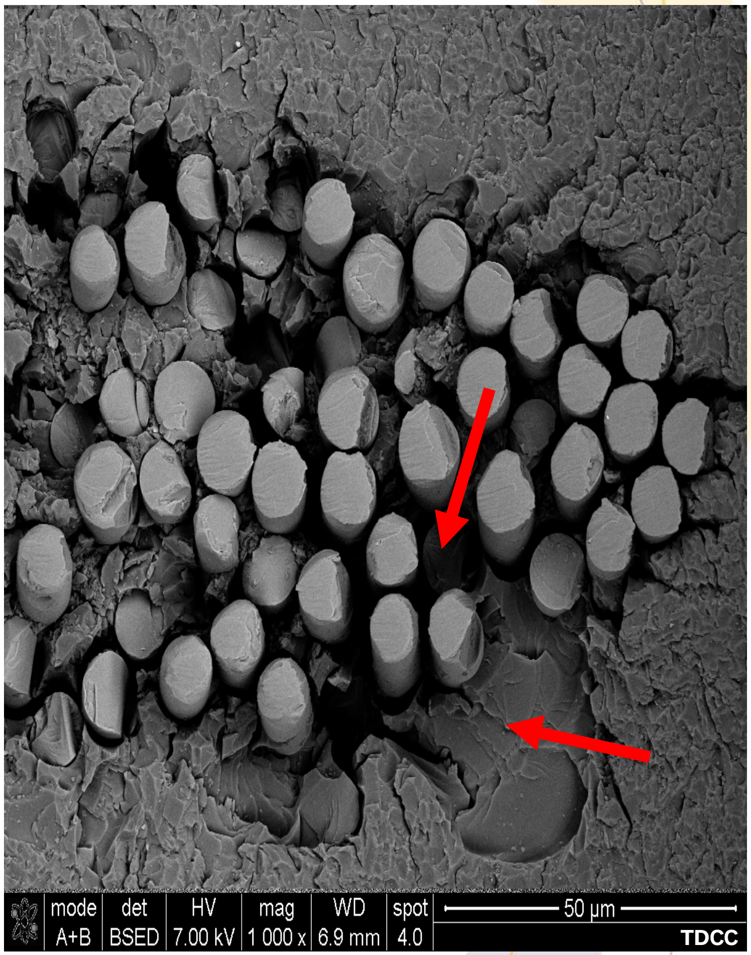




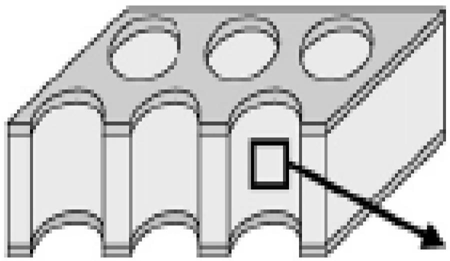
Non-toughened Laminate – (non-toughened) Control (formulation # 5)

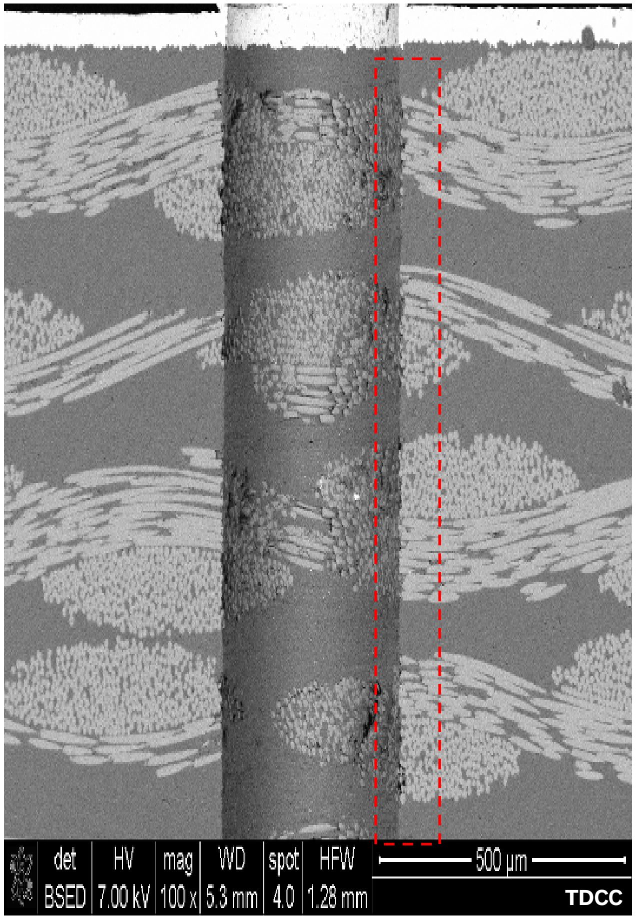


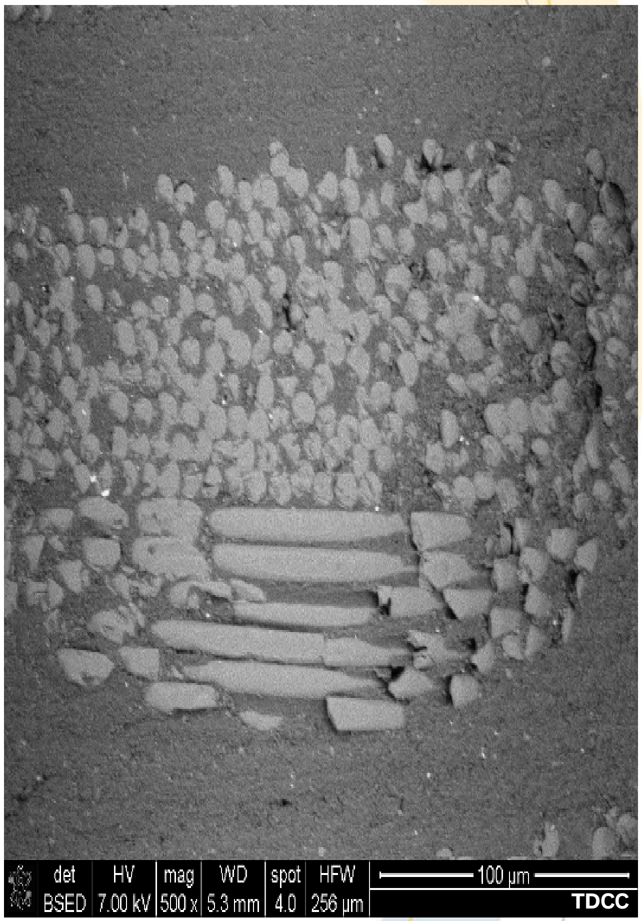




TA1 Toughened Laminate (TA1 Toughened) (formulation # 4)

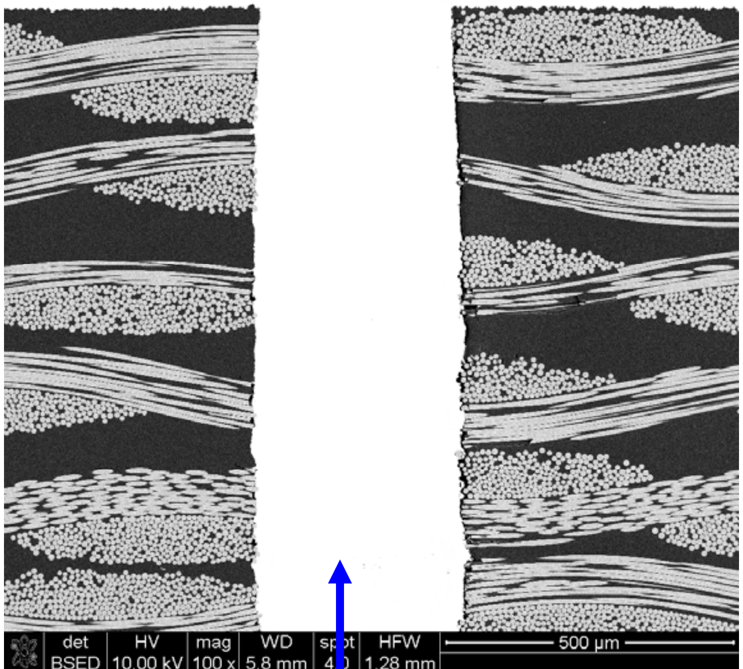






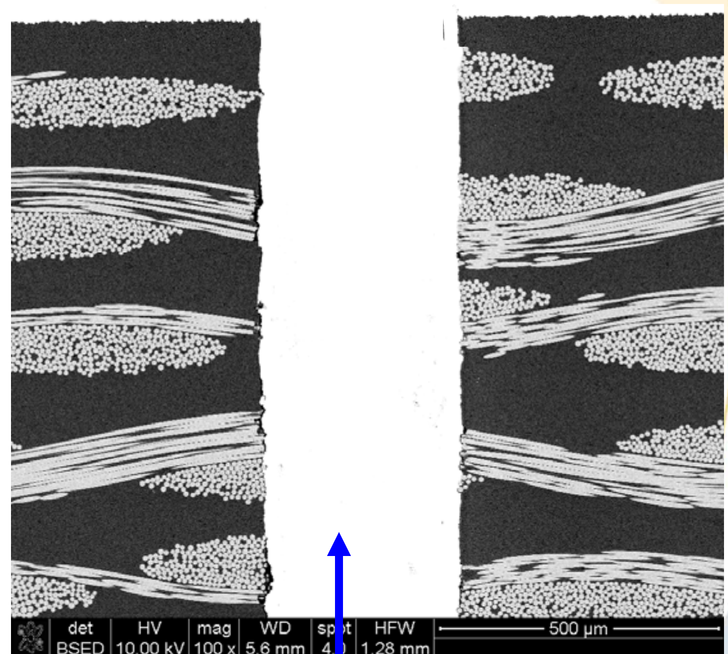
Surface Roughness of Plated Through Holes

Control



PTH

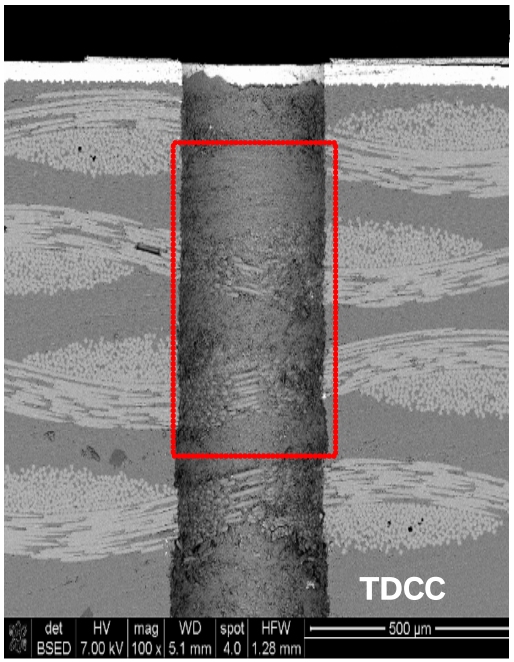
TA1 Toughened

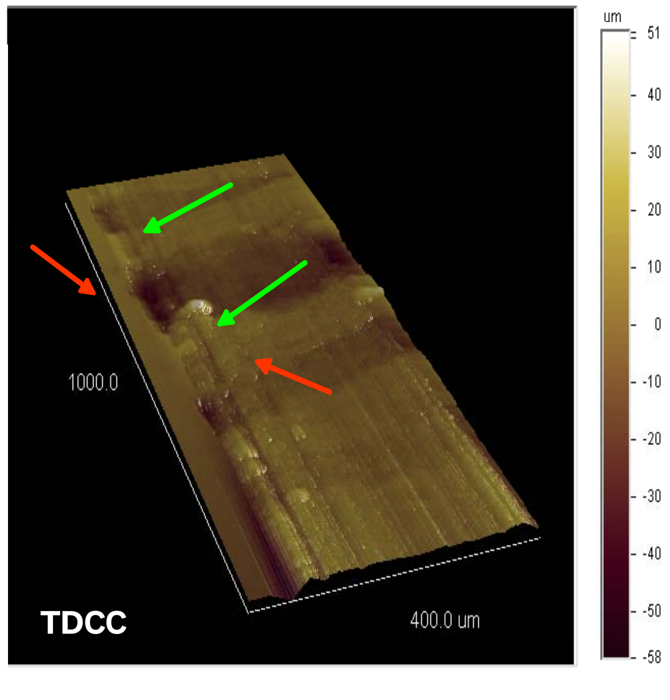


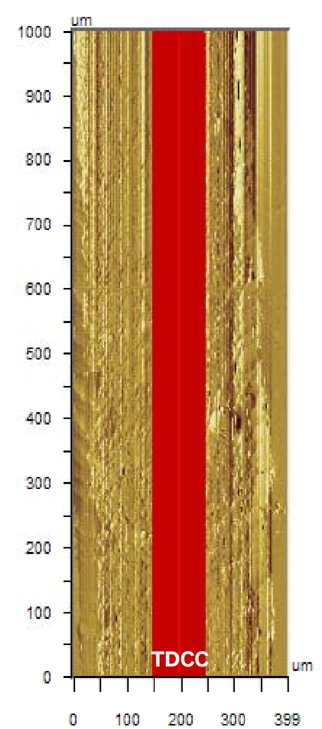
PTH

PTHs may mask surface defects thus trapping voids

Evaluation of Drill Hole Surface Roughness

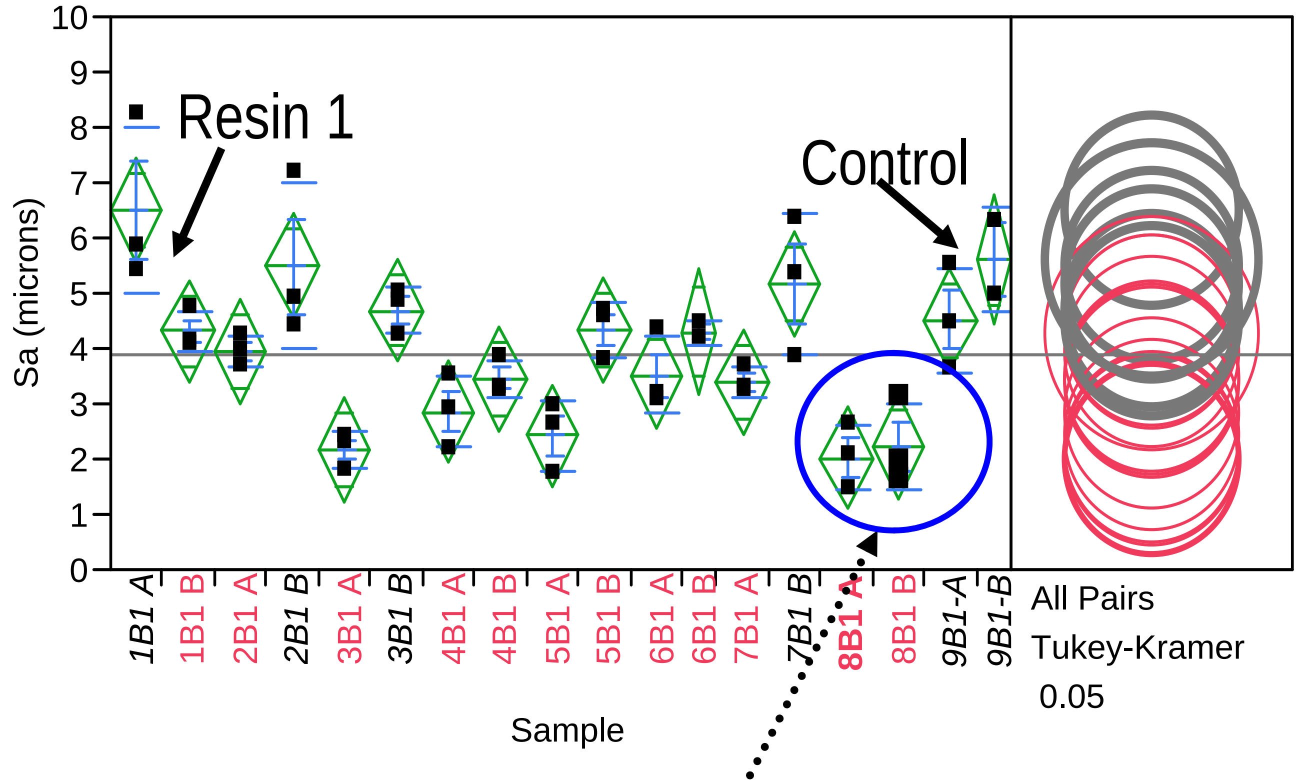






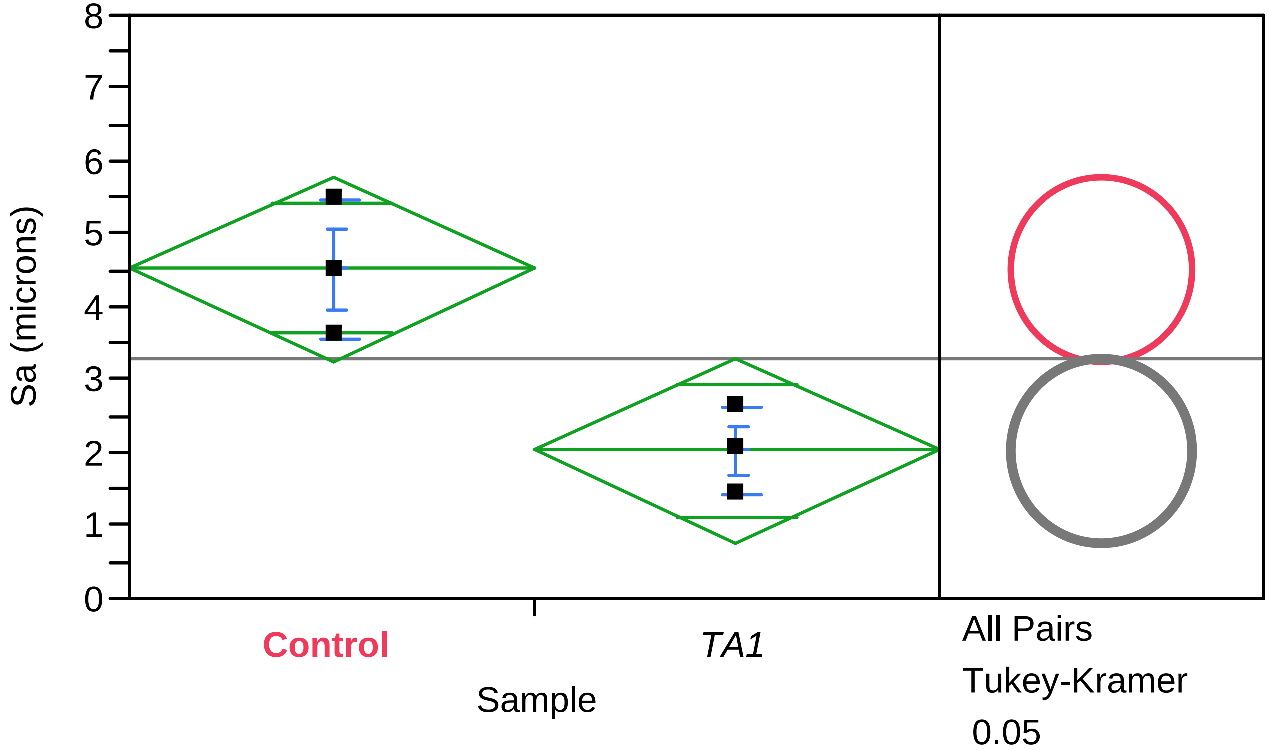
$$S_a = \frac{1}{MN}\sum_{k=0}^{M-1}\sum_{l=0}^{N-1}\left|z(x_k, y_l) - \mu\right|$$

Average Surface Roughness of Drill Holes for Different Formulations



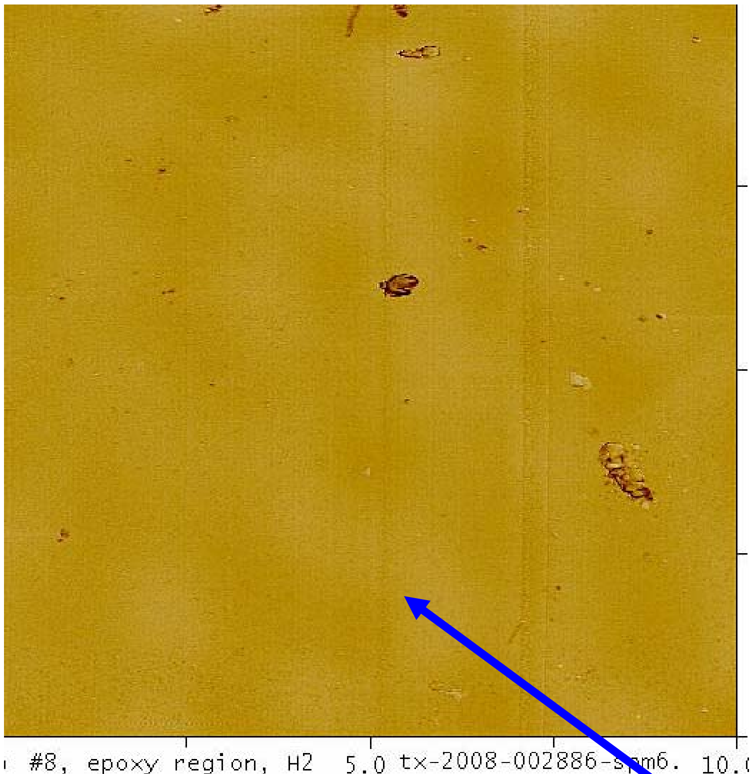
TA1-toughened system exhibits lowest roughness compared with the other formulations

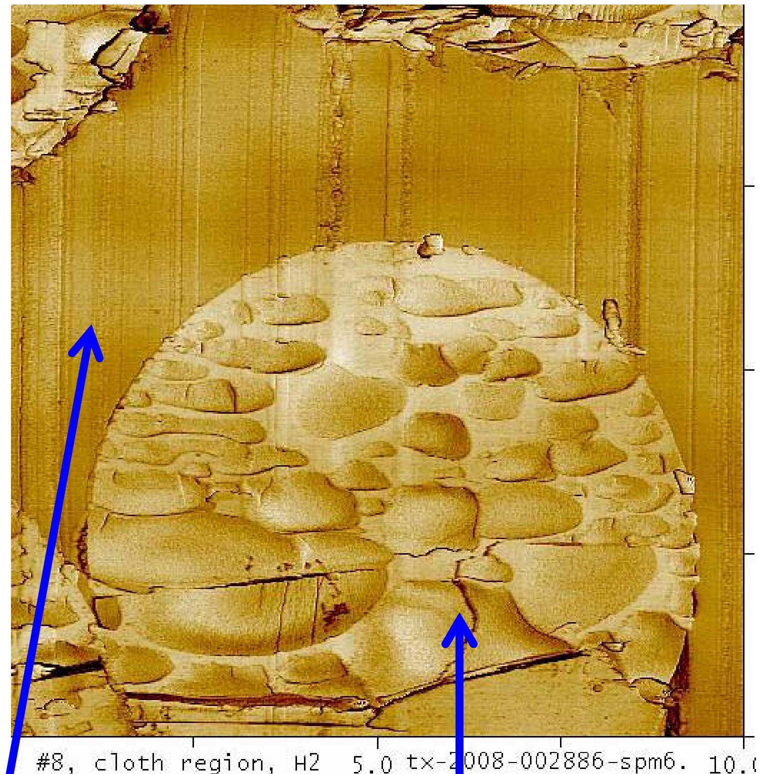
Evaluation of Surface Roughness for Toughened and Non-toughened Systems



The TA1-toughened formulation exhibits significantly lower surface roughness than the non-toughened control sample

Dispersion of Toughener Particles in Laminate - Control

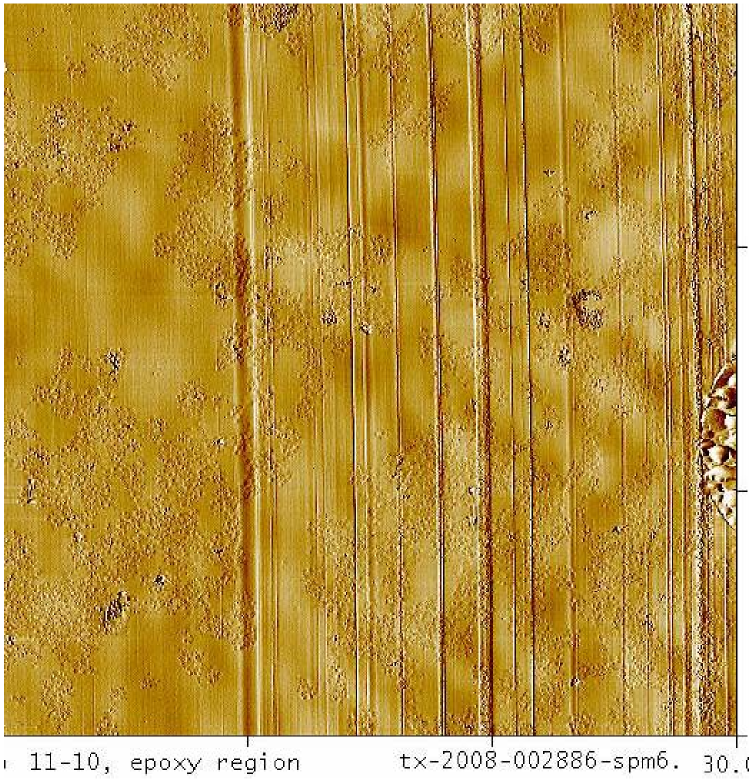


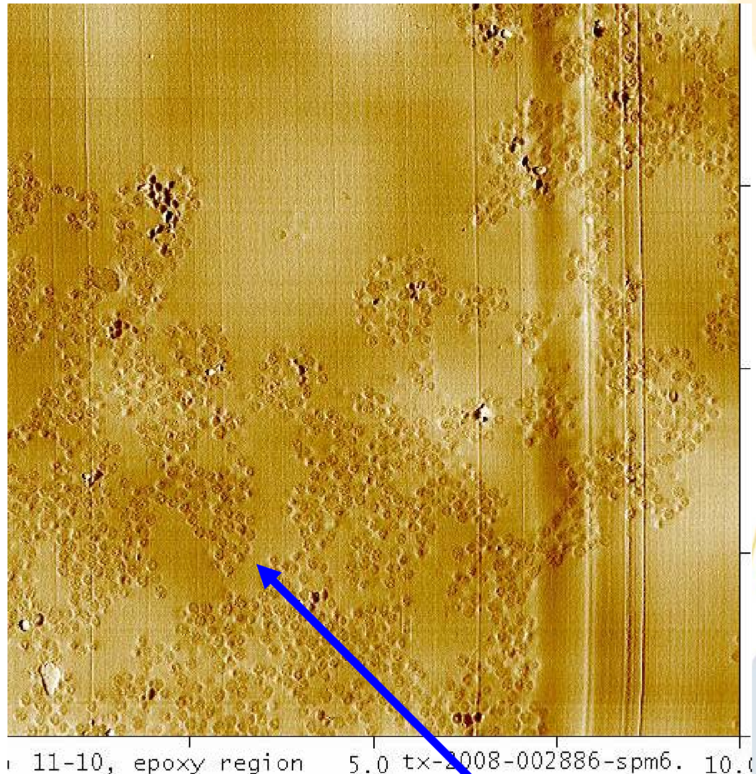


Bulk resin

Single fiber

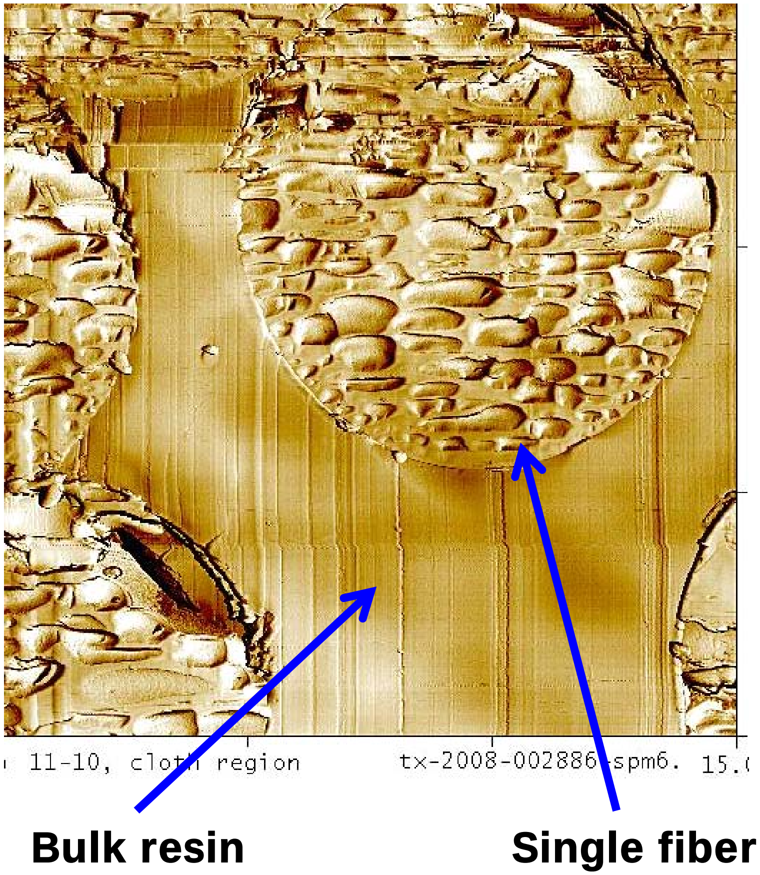
Dispersion of Toughener Particles in Laminate – TA2 (bulk resin)

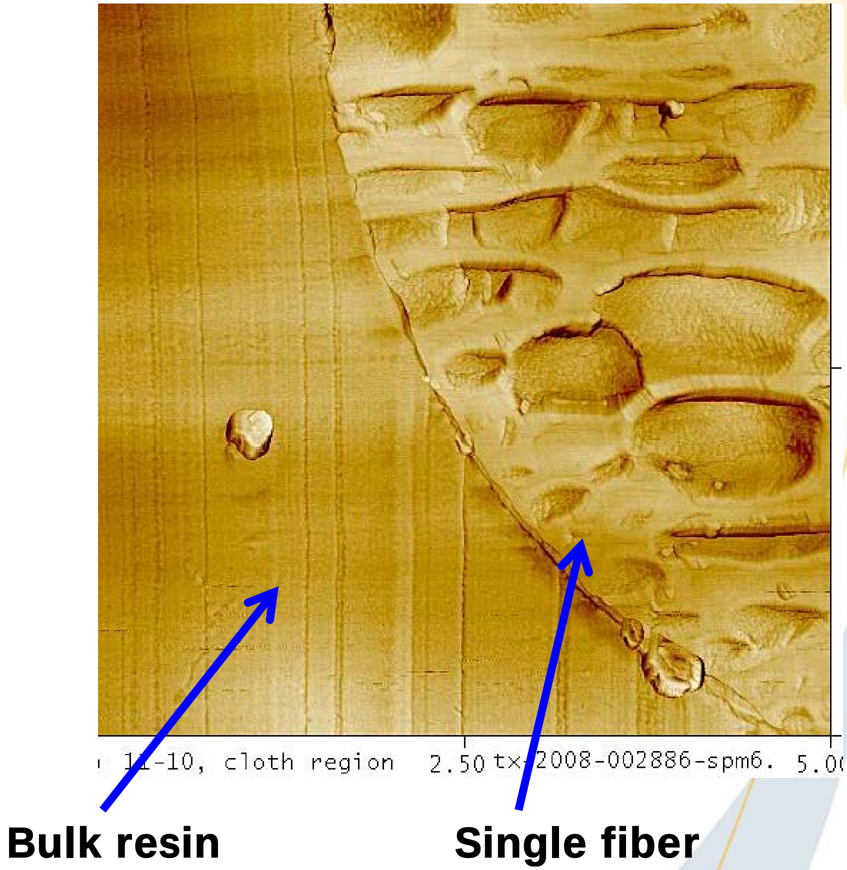




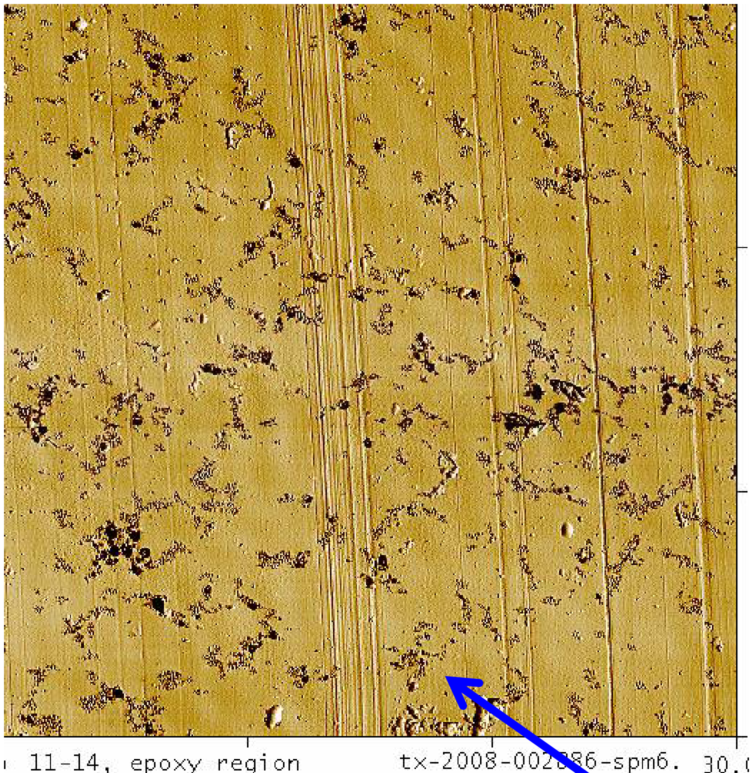
Clusters of toughener

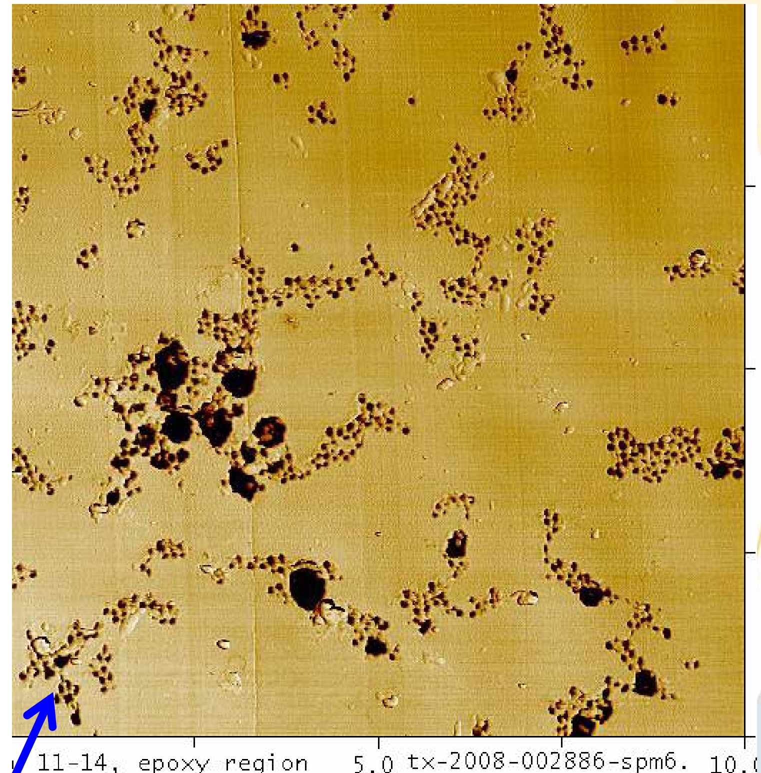
Dispersion of Toughener Particles in Laminate – TA2 (fiber tow)





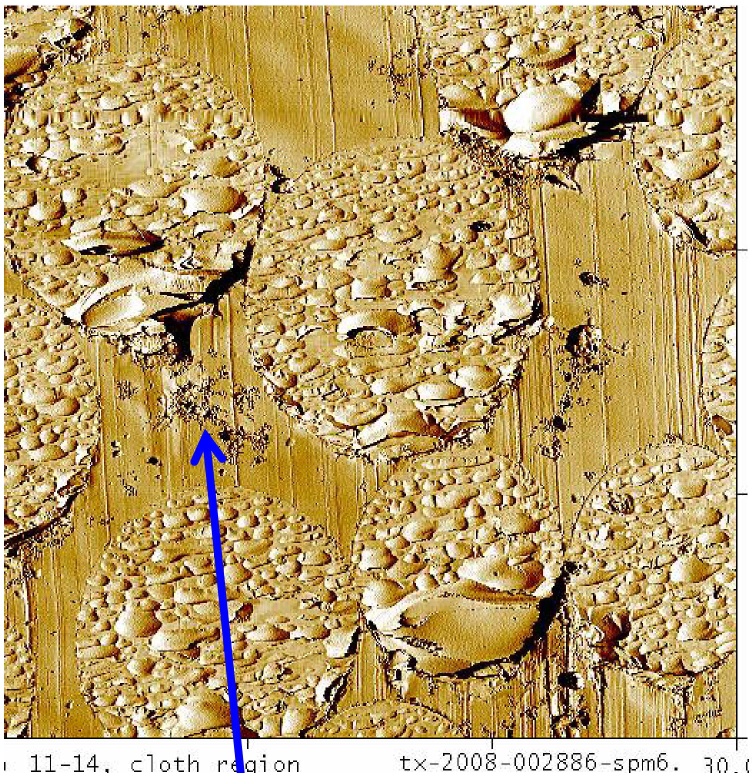
Dispersion of Toughener Particles in laminate – TA1 (bulk resin)



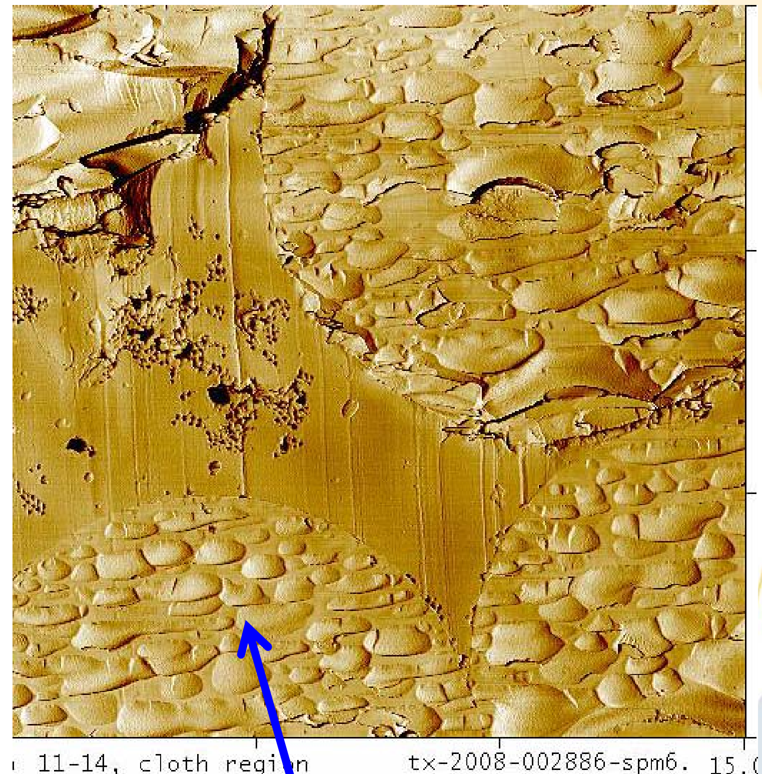


Toughener particles

Dispersion of Toughener Particles in Laminate – TA1 (fiber tow)

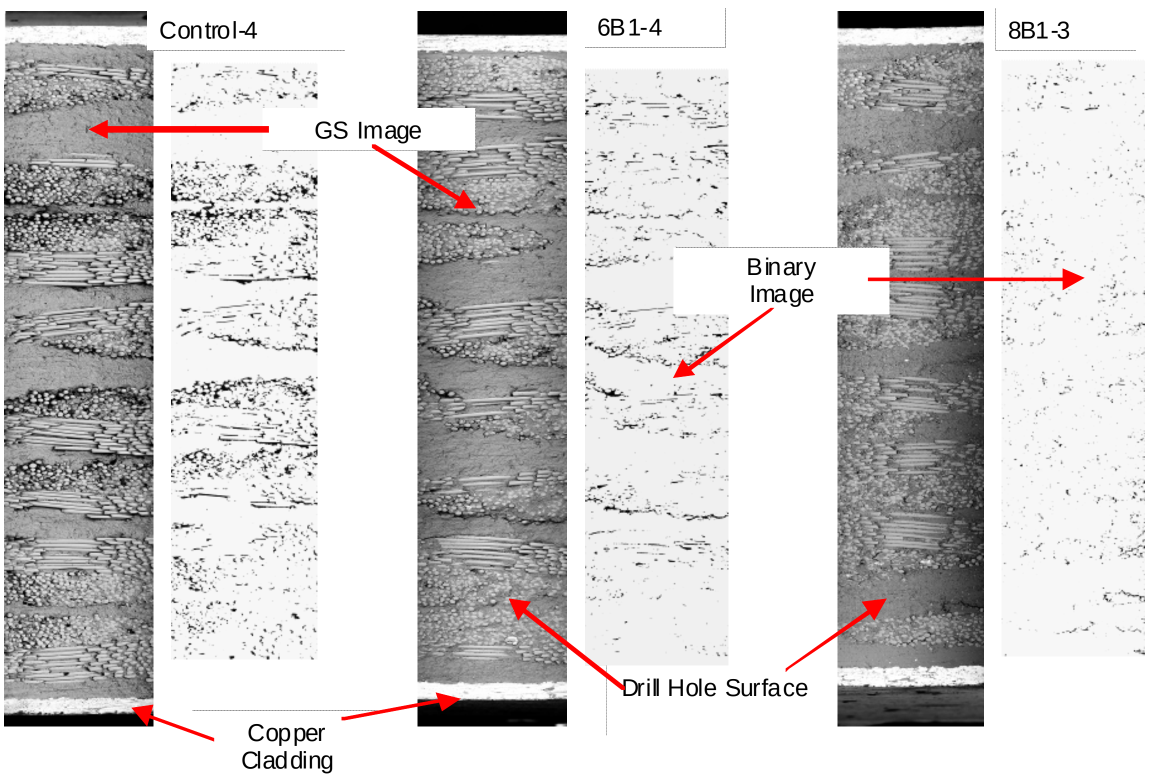


Toughener particles



Single fiber

Quantification of Drill-hole Surface Defects



Irregular Shape	Equivalent Circle

Irregular Shape	Equivalent Circle
Area = 4805px	Area = 4805px
Length = 141px	Diameter = 78px
Width = 59px	
ECD = 78px	

$$ECD = 2 \times \sqrt{A/\pi}$$

Summary

- **Brittle failure is observed subsequent to drilling of a non-toughened resin**
- **Toughening agents *TA1* and *TA2* disperse very well in an epoxy resin**
- **Drill-hole surface quality significantly improves with the incorporation of *TA1* into an epoxy formulation**
- **Drill-hole surface quality deteriorates with increasing temperature of the drill-bit**
- **Fracture toughness evaluations must be performed at high strain rates consistent with the high strain rates of the drilling process**

Toughener Offering

- ***TA1* is currently experimental material, available in limited quantities**