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Developmental Halogen-Free High Performance Dielectric Substrates (with Different Reinforcement Supports) for the PCB/HDI and High-Frequency Applications

David K. Luttrull, Fred E. Hickman III, and Joseph Bauler
Park-Nelco, Neltec Business Unit
Tempe, Arizona

Abstract
This paper presents a comparison of several resin systems on different support reinforcements including on Thermount®[1] (or NWA), E-Glass (or E), and NE-Glass[2] (SI™) (or NE). The resin systems compared in this paper include D5300[1] (Halogen-Free, High T_g or HFHT), N4000-13 (high-speed/low-loss or HSLL), and N4000-6 (high T_g FR4 or HTFR). It is proposed that the HFHT resin can be used for high-signal speed applications, chip-test boards, and in some cases, lead-free solder PCB processes. The parameters compared herein include thermal, mechanical, dielectric (i.e., stripline tests), flame-retardant character, and cure profile characteristics. This study gives the chip-test board, backplane, and wireless base-station designer valuable information concerning the functionality of these resin systems with different support reinforcements.

Introduction

The design groups and OEMs are increasingly designing devices that have material requirements that challenge the current PCB supply companies, including laminate suppliers. Once the requirements that are increasing are the need for substrates that have lower dielectric constants (K, ε_r, or D_k) and lower dielectric loss (i.e., loss tangent or dissipation factor, D_f). This increasing need for low D_k materials is due to the fact that signal speeds are increasing for a variety of reasons. The other reason for the need of a lower D_k thin-layer material is to decrease the thickness (or size) of the PCB. The low D_f becomes important for wireless applications, digital broadband, and optical-data servers.

Devices such as cellular phones require micro-via formation using laser drills. Thus, these types of HDI devices require materials that are easy to laser drill. In addition, high-density designs that have components very close together, require low coefficients of thermal expansion to improve production yields and in some cases, enhance the device operation over various temperature ranges (i.e., chip-test boards).

Finally, there is increasing pressure to employ environment-friendly processes and building blocks in all industries. It is believed by some that effluent emitted from the burning of old circuit boards containing halogenated additives (used for flame retardancy requirements to gain UL 94VO recognition) can cause health problems. In addition, the PCB industry is moving to the use of lead-free soldering.[3]

In this paper we attempt to present test results, discuss and compare materials that address many of the future needs discussed above.

Results

We have chosen to look at four (4) different resin systems on three (3) different reinforcements. The resin systems and reinforcements studied are shown in the matrix below in Table 1:

We arbitrarily show the HTFR-NWA laminate as the "Control", because this type of material reinforced with NWA is used in the highest volume and happens to be used for cellular phone applications. Laminate suppliers also sell NWA/polyimide and epoxy materials for applications in the following markets: military, avionics, telecomm infrastructure, automotive and -test board builds. The results of tests on the HSLL-E laminate materials are shown in Table 2 on the next page with the HTFR-NWA laminate as the "Control."

We have found that in the case of epoxy supported with NWA, flame retardancy is proportional to the amount of entrained moisture in the laminate. Thus, as the material becomes drier, the material tends to burn longer.

Table 3 shows the comparison of the developmental halogen-free, high T_g resin system (HFHT) on different reinforcements as compared to the Control, (HTFR-NWA laminate).

Table 1 – Materials Discussed

Reinforcement → Resin ↓	Woven E-Glass (E) 2116	NE 2116	4 mil nwa
HFTR (Multifunctional Epoxy)	None	None	**CONTROL** HTFR-NWA *Cellular Phones/HDI*
HSLL (Enhanced Epoxy, Low D_k/D_f)	HSLL-E *High-Speed Substrate*	HSLL-NE *High-Speed/Low Loss-Substrate*	HSLL-NWA *High-Speed/Low-Loss/HDI, HDI*
HFHT (Halogen-Free, Low D_k)	HFHT-E *High T_g, Halo-Free*	HFHT-NE *High T_g, Halo-Free, High Speed*	HFHT-NWA *High T_g, Halo-Free, High Speed, HDI*
(Polyimide)	Polyimide-E *High T_g, Thermal Resistant*	Polyimide-NE *High T_g, Thermal Resistant*	Polyimide-NWA *High T_g, Thermal Resistant, HDI*

Table 2 - HSLL Resin on Different Reinforcement Supports

Material ®	**Htfr-NWA Control**	**HSLL-E**	**HSLL-NE**	**HSLL-NWA**
Reinforcement ®	NWA	E-Glass (E)	NE	4 MIL NWA
Test Parameters				
Glass Transition, T_g				
T_g °C by DSC	170	213	213	207
T_g °C by TMA	160	200	200	195
Thermal Expansion				
Z-CTE (50 to 288 °C)	5.7%	5.2%	5.2%	4.2%
X/Y-CTE	10–14 ppm	10–14 ppm	10-14 ppm	10-14 ppm
T260 (Delam. Time)	No delam.	No delam.	No delam.	No delam.
T300	2.0 min.	4 min.	4 min.	4 min.
TGA (Temp at 5% wt loss in °C)	395	360	360	373
Dielectric Tests				
D_k/D_f,(RC = 55 ±2%)				
1 MHz	3.9/0.021	3.7/0.008	3.4/0.008	3.3/0.011
2.5 GHz	3.3/0.031	3.6/0.013	3.3/0.009	3.2/0.012
10 GHz	3.3/0.027	3.5/0.013	3.3/0.010	3.1/0.012
Mechanical Tests				
Copper Peel Strength (lb/in)	8.6	9.6	9.6	7.6
Inner-laminar Bond Strength (lb/in)	7.5	5.2	5.2	8.5
UL Flame Rating Test (50 sec total maximum burn time on 5 samples)	94V0*	94V0	94V0	94V0

Table 3 - HFHT Resin on Different Reinforcements

Material ®	**HFTR-NWA** **Control**	**HFHT-E**	**HFHT-NE**	**HFHT-NWA**
Reinforcement ®	4 MIL NWA	E-Glass (E)	NE	4MIL NWA
Test Parameters				
Glass Transition, T_g				
T_g °C by DSC	170	189	186	182
T_g °C by TMA	160	181	187	178
Thermal Expansion				
Z-CTE (50 to 288 °C)	5.7%	4.2%	4.2%	4.6%
X/Y-CTE	10–14 ppm	18-19 ppm	18-19 ppm	10-14 ppm
T260 (Delam. Time)	No delam.	No delam.	No delam.	No delam.
T300	2 min.	3 min.	6 min.	3 min.
TGA (Temp at 5% wt loss in °C)	395	397	388	395
Dielectric Tests				
D_k/D_f,(RC = 55 ±2%)				
1 MHz	3.9/0.021	4.3/0.014	3.8/0.010	3.3/0.011
2.5 GHz	3.3/0.031	3.5/0.015	3.2/0.015	3.3/0.019
10 GHz	3.3/0.027	3.5/0.015	3.2/0.016	3.2/0.019
Mechanical Tests				
Copper Peel Strength (lb/in)	8.6	8.8	9.7	7.6
Inner-Laminar Bond Strength (lb/in)	7.5	5.7	5.3	8.5
UL Flame Rating (50 sec total maximum burn time on 5 samples)	94V0	94V0	94V0	94V1 0.031” 94V0 0.010”

Table 4 - Pure Polyimide Resin on Different Reinforcements

Material ®	**HTFR-NWA Control**	**Polyimide -E**	**Polyimide -NE**	**Polyimide -NWA**
Reinforcement ®	4 MIL NWA	E	NE	4 MIL NWA
Test Parameters				
Glass Transition, T_g				
T_g °C by DSC	175	260	260	260
T_g °C by TMA	160	248	248	249
Thermal Expansion				
Z-CTE (50 to 288 °C)	5.7%	2.7%	2.7%	2.9%
X/Y-CTE	10–14 ppm	12-15 ppm	12-15 ppm	10-14 ppm
T260 (Delam. Time)	No delam.	No delam.	No delam.	No delam.
T300	2 min	No delam.	No delam.	No delam.
TGA (Temp at 5% wt loss in °C)	395	450	452	445
Dielectric Tests				
D_k/D_f,(RC = 50 ±2%)				
1 MHz	3.9/0.021	4.1/0.008	3.6/0.007	3.5/0.013
2.5 GHz	3.3/0.031	3.8/0.013	3.3/0.012	3.2/0.014
10 GHz	3.3/0.027	3.8/0.011	3.3/0.009	3.2/0.015
Mechanical Tests				
Copper Peel Strength (lb/in)	8.6	9.6	8.6	7.6
Inner-laminar Peel Strength (lb/in)	7.5	5.6	8.0	9.4
UL Flame Rating (50 sec total maximum burn time on 5 samples)	94V0	94V1	94V1	94V1

Discussion

Dielectric Behavior

The dielectric constant (D_k) and dissipation factor of the circuit board and antennae substrates are extremely important parameters for building devices. For a given impedance the thickness of the dielectric layer depends on the D_k. Thus, the D_k is one major parameter that sets the limit of circuit and layer density. On the other hand, the dissipation factor or the tendency of the dielectric substrate to internally convert the signal energy into heat, effects the power use and management by the device and creates bandwidth limitations (i.e., digital broadband devices). In antennae, the dissipation factor (or *loss tangent* as used by the RF/Microwave engineer) is the performance parameter.

The dielectric response of the materials has been plotted for convenience of review, where the low frequency and high frequency was plotted. The test methods for the D_k and D_f were *impedance analyzer* method and *stripline* method, both IPC-TM-650 procedures. In general, as the frequency of the energy moving across the dielectric substrate increases, the D_k will decrease. The results of the tests shown below show this phenomenon as expected. However, the resin/reinforcement composite appear to drastically affect the relative steepness of this profile. For example, the HSLL-E and the HSLL-NWA materials appear to have the some slope or profile over the frequency range shown. However, the HSLL-NE laminate appears to have a fairly flat D_k response over frequency. The HTFR-NWA substrate behaves very strangely, where the D_k drops radically between 1 MHz and 2.5 GHz, but then stays flat out to 10 GHz.

In summary, Figure 1 shows that the HSLL resin has a D_k, which is predictable (or linear) over frequency, regardless of reinforcement composition. This data helps verify why HSLL-E is such a good high-speed/low-loss dielectric resin substrate and gaining in usage. On the other hand, the other resin D_k's appears to change radically between 1 MHz and 2.5 GHz (2,500 MHz).

In Figure 2, the D_k of the Halogen-Free resin on NWA, designated as HFHT-NWA, appears to be altered the least by the increase in frequency from 1 MHz to 2.5 GHz. The Halogen-free resin on both of the reinforcements NE and E-Glass show a dramatic change between 1 MHz and 2.5 GHz, but they remain flat out to 10 GHz. Here, as expected, the NE reinforcement support gives a lower D_k at the higher frequencies than the E-Glass. Finally, it is interesting to note that Figure 2 shows that the HTFR-NWA, the HFHT-E and the HFHT-NE laminate materials all show a large and comparable drop in D_k when the frequency is changed from 1 MHz to 2.5 GHz.

In Figure 3 one can see that the Polyimide exhibits a drastic drop in D_k as the frequency of the signal increases from 1 MHz to 2.5 GHz. The Polyimide-E substrate shows the biggest "dive" in D_k. However, regardless of the reinforcement, the D_k is flat at the higher frequency range from 2.5 GHz to 10 GHz.

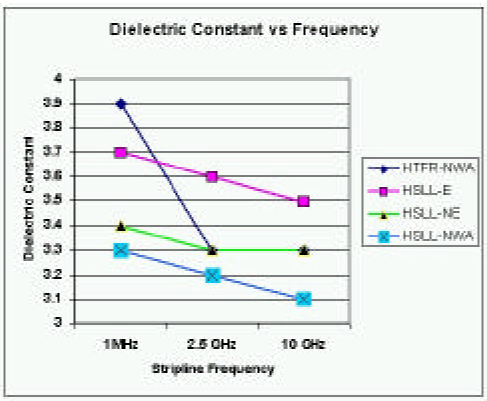

Figure 1 - HSLL Dielectric Constant vs. Frequency

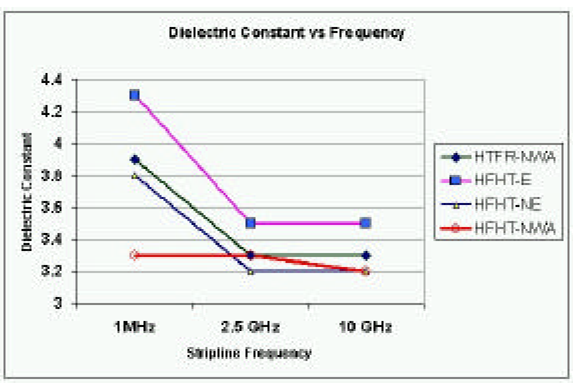

Figure 2 – HFHT dielectric Constant vs. Frequency

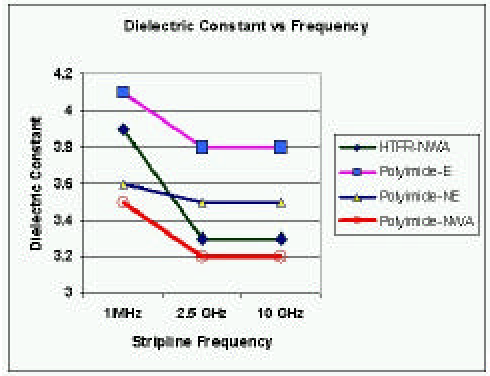

Figure 3 – Polyimide Resin Dielectric Constant vs. Frequency

Dissipation Factor (D_f)

In general, as the frequency and thus, energy increases through a dielectric substrate, the D_f should increase. Thus, D_f has an inverse relationship to frequency or signal energy. In reviewing Figure 4 (below), it is evident that NWA and NE reinforcements provide the flattest response over a wide range of frequencies. Thus, this would be a good digital broadband device dielectric. Interestingly, the HTFR-NWA and the HSLL-E laminate give a higher D_f at 2.5 GHz than at 10 GHz. We

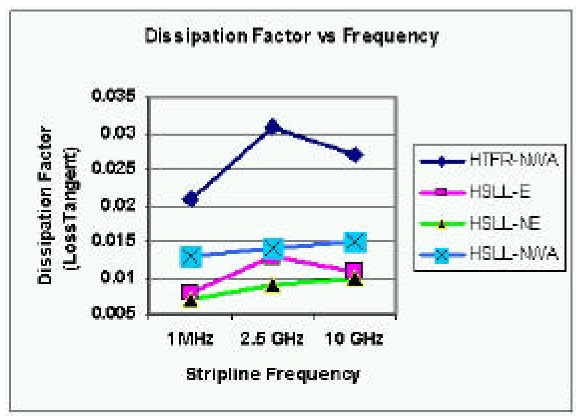

Figure 4 – HSLL Dissipation Factor vs. Frequency

Mechanical Properties

The bond strengths of both the copper peels (resin/copper) and the inner-laminar bond (resin/reinforcement) was plotted. The copper peels are stronger in all cases with the HSLL-based laminates, except in the case of the HSLL-NWA material. Here the inner-laminar bond (resin/reinforcement) strength is higher than it is on both the E-Glass and NE reinforcements.

As with the case of the HSLL resin and the HSLL-NWA laminate, the HFHT-NWA shows a higher inner-laminar bond than a copper peel. The Bromine-free HFHT-NWA also shows higher inner-laminar bond strength than the HTFR-NWA laminate material. The weakest inner-laminar bond strength in the case of the Bromine-free HFHT resin system is on the NE reinforcement version. Figure 5 - High-Speed/Low-Loss

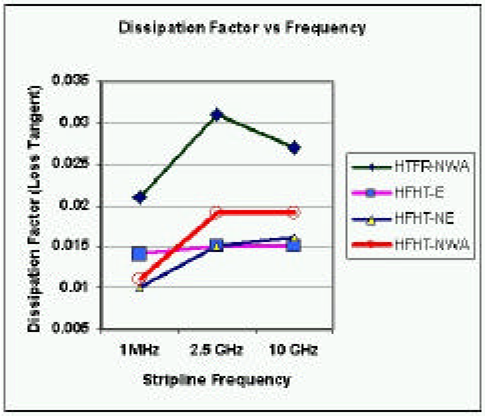

Figure 5 – HFHT Dissipation Factor vs. Frequency

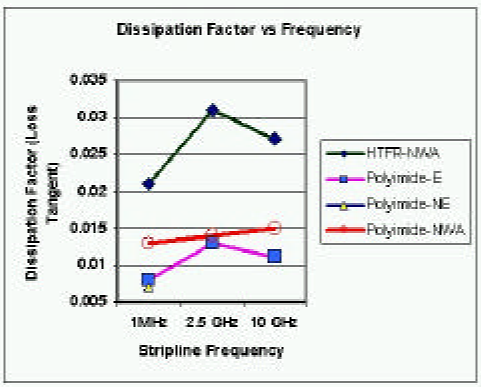

Figure 6 – Polyimide Dissipation Factor vs. Frequency

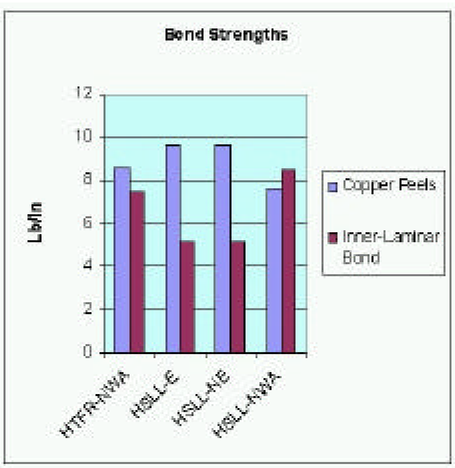

Figure 7 – HSLL Bond Strength

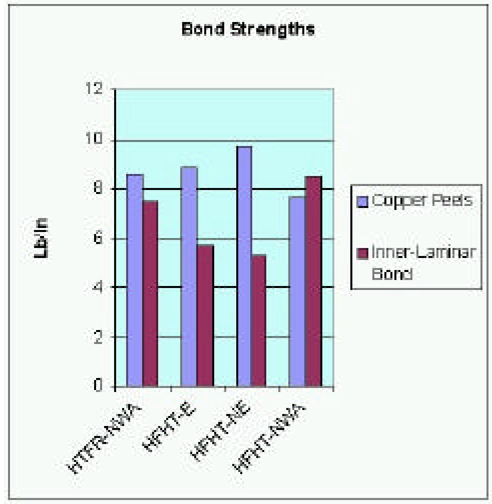

Figure 8 – HFHT Bond Strenght

Figure 9 displaying the Polyimide resin on different reinforcements again illustrates the fact that the inner-laminar bond strength (resin/reinforcement) is stronger than the copper peel strength. It is also interesting to note that the Polyimide-NE has a much higher inner-laminar bond strength (resin/reinforcement) than does this resin on E-Glass. This inner-laminar bond difference in the case of Polyimide could be related to the fact that the E Glass uses a glass finish from the U.S., while the NE reinforcement uses a Japanese glass finish. Thus, it could be a finish compatibility issue. As far as we know, there is no finish applied to the NWA reinforcement.

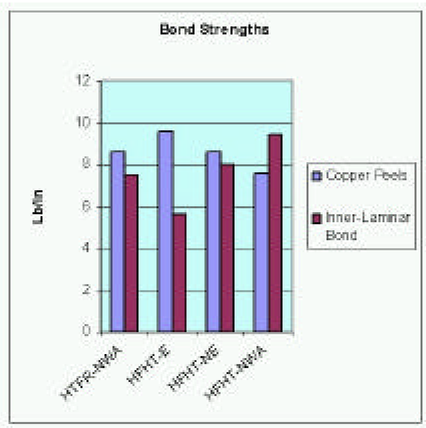

Figure 9 – Polyimide Bond Strengths

Cure Profile Comparisons

The cure profiles of the various prepreg materials we have discussed were measured using an advanced polymer analyzer or APA, by Alpha Technologies, Model APA2000. The primary parameters we looked at include the elastic modulus (G') and the viscosity (n'). The APA instrument is able to measure the visco-elastic properties of resins and reinforced resins beyond the cure point. The APA is a useful tool for evaluating the cure profile of a material as a function of predetermined thermal cycle. The difference from a "true" press cycle is that the APA applies only a few pounds of force on the prepreg coupon.

Figure 10 shows the gel time (minutes) as determined by time to reach a maximum viscosity, after which point the viscosity becomes undefined. Each material has their own characteristic press cycle cure temperature, but the heat rise used for all materials was 6 °F/min. It is clear from the Figure (10) that the gel times are shorter for polyimide, the low-D_k/low-D_f epoxy (HSLL) and the high Tg halogen-free (HFHT) resin. The largest differential between gel times on NWA versus E-Glass was for the HFHT resin.
Figure 11 shows the maximum elastic modulus along the cure profile of the materials studied here. For the low-D_k/low-D_f epoxy (HSLL) and the Polyimide resins, the modulus (G') is higher for the E - reinforced material as expected. The halogen-free material showed the moduli to be about the same for the E-Glass- and NWA-reinforced and similar to the HTFR-NWA laminate used in cellular phones.

Since it appeared that the higher T_g materials also had higher cured moduli, we plotted the profile of the elastic moduli against the T_g (DSC) of each material. This relationship is shown in Figure 12 (below). As expected the G' and the T_g are proportional to each other.

Intuitively, this makes sense since most high Tg materials tend to be "brittle", while the lower Tg materials tend to be "tough" or more rubbery.

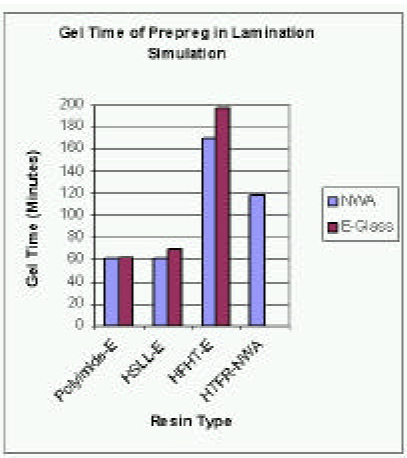

Figure 10 – Prepreg Gel Time

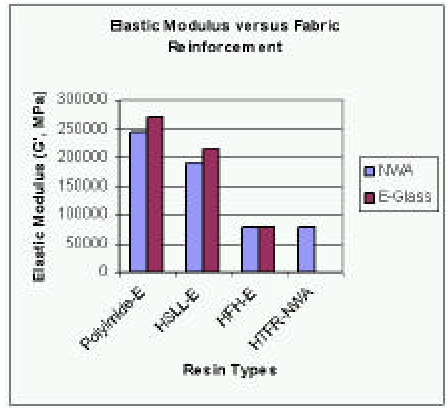

Figure 11 - Maximum Elastic Modulus

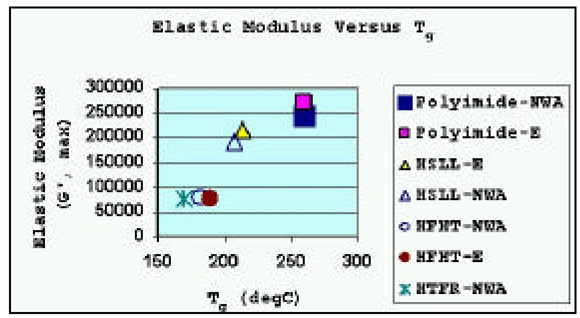

Figure 12 - G' (Elastic Modulus from APA) vs. Tg using DSC

Conclusions
The HSLL-NWA material has several advantages over HTFR-NWA: Namely the enhanced dielectric properties and the higher T_g. For the HSLL-NWA, the D_k is low and linear over a wide range of frequencies (1 MHz to 10 GHz). Since the HSLL-NWA has a low D_k, it can be used to make thinner dielectric layers for the same impedance.

The halogen-free material studied here, HFHT-NWA, gave a low D_k (3.2) and flat D_k over wide range of frequencies. The flame retardancy is a little weak for 94V-0 (64sec versus the 50 sec maximum for a 0.031" core), but the thinner constructions were 94V-0. The halogen-free material we studied has a higher T_g than halogen-free materials on the market today, but being a high-technology product, it is more expensive than the halogen-free "FR4" offerings.

The Polyimide studied, showed an extremely stable and low loss (D_f) over a wide frequency range.

From the comparison of the APA polymer analyzer results (visco-elastic properties) and the T_g of the materials, it is clear that the "toughest" materials (lowest G') have the lower T_gs. These resin materials are HTFR and HFHT, which are primarily epoxy. The next "toughest" resin system is the HSLL, and the most "brittle" material was the Polyimide, which is not surprising, until you see (Figure 9) that indicates that the inner-laminar bond strength on NWA is the highest!

Figures 13 and 16 shows that the HFHT resin has the "best" kinetic properties (n' or viscosity profile) of the materials discussed. Generally, the more "drawn out" or the more gradual the n' vs. time (or temperature) profile, the better the bond-ply material behaves in terms of filling circuitry and minimizing the chance for dryness and resin voids.

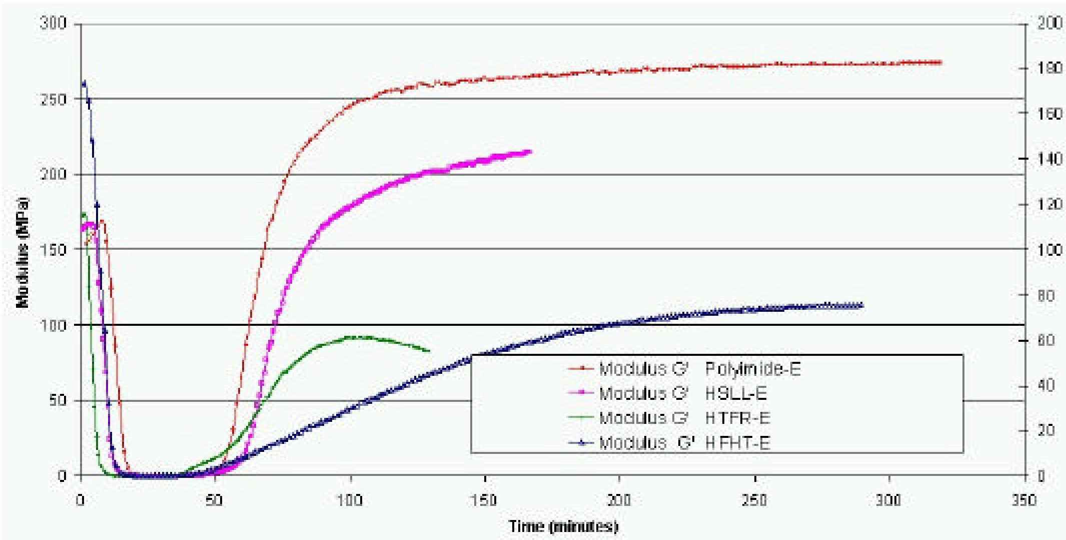

Figure 13 – APA Cure Profile, E-Glass Comparisons

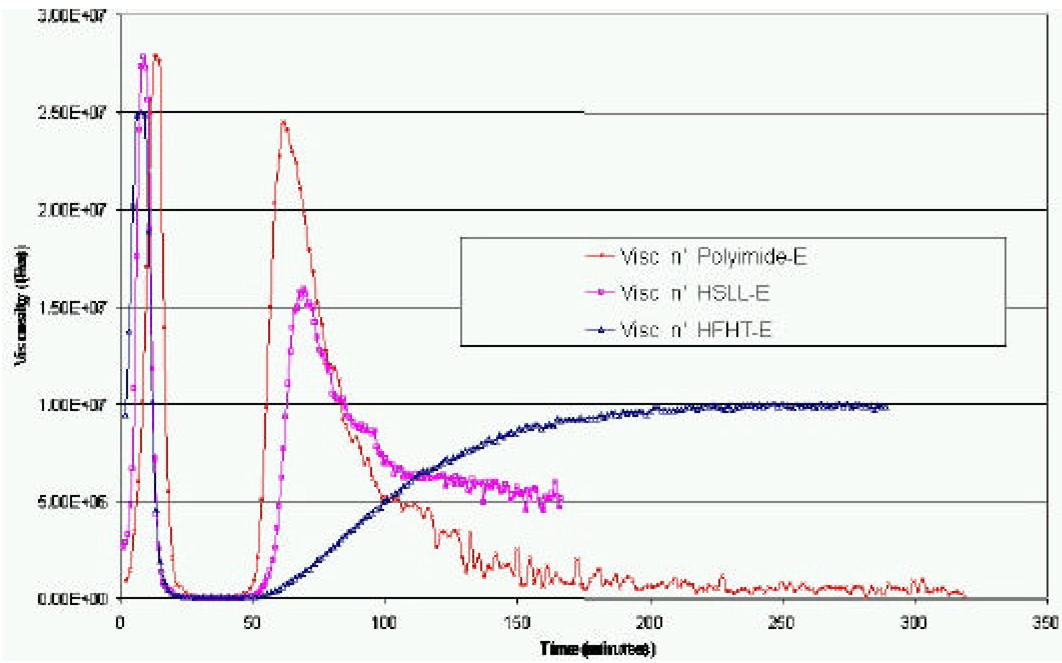

Figure 14 –APA Cure Profile – Viscosity E-Glass Comparisons

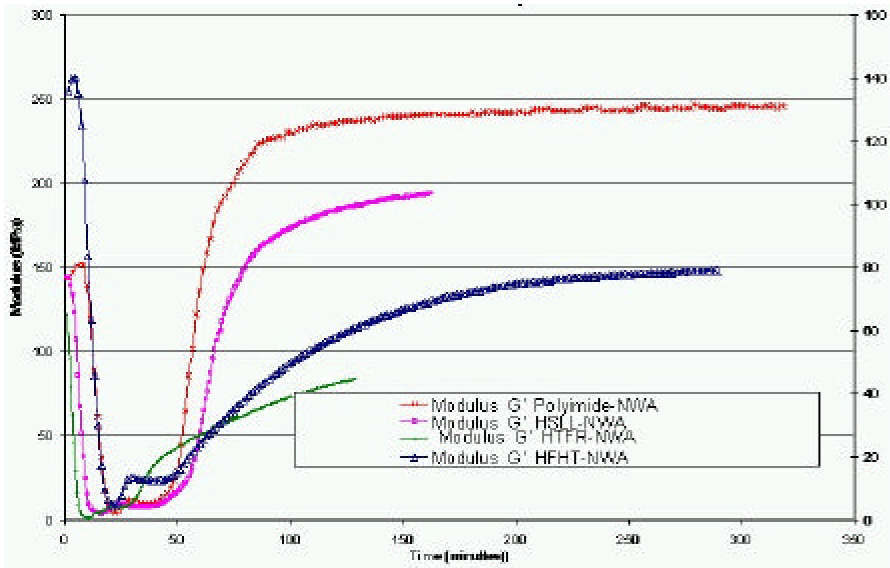

Figure 15 – APA Cure Profile NWA Comparisons

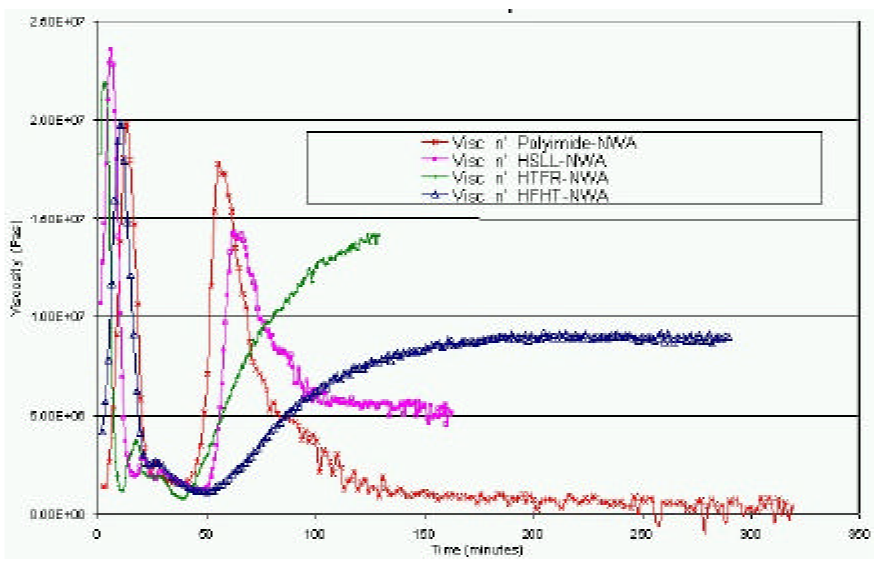

Figure 16 – APA Cure Profile – Viscosity NWA Comparisons

All materials studied appeared to cure faster from the B-Stage to the C-Stage on NWA, than the comparable E-glass reinforced versions. There, gel time differences were not huge, but they were noticeable.

Concerning the mechanical properties, the materials supported by the NWA all showed higher inner-laminar bond strength (resin/reinforcement) than copper peel strength (resin/copper). The "control", HTFR-NWA, was different in this regard, where the copper peel was a little higher than the inner-laminar bond strength. The most surprising results in the mechanical property area were that the material with the highest inner-laminar bond strength was polyimide-NWA. All of the materials showed strong copper peel strengths.

We did not laser drill these materials. This would be the next logical set of tests to perform on these materials.

The materials reinforced with the NWA should be extremely CAF (conductive anodic filament) growth resistant, since there are no glass fiber pathways for a copper filament to grow. These tests are in progress and may be available by the time of the presentation at the IPC Expo-2002 in California in March, 2002.

We did not observe measurable differences in the x- and y-CTE values between the NWA and the glass reinforcement compositions. We expected to see a lower CTE for the NWA in the laminate plane than for the woven glass reinforcements. This is either not the case, or our measurement techniques need some improvement in this area.

References

1. "New Halogen-Free PCB Materials for High-Speed Applications and Lead-Free Solder Processes," David K. Luttrull and Fred E. Hickman III, Future Circuits International, March 2001.
2. Matsumoto, M., Suzuki, Y., et al., "New Low Dielectric Glass Fiber Woven for the Next Generation Board," JPCA (Meeting), June 1999.
3. "Lead in the Crosshairs," IPC Review, pp14-16, December 1999.; "Get the Lead Out," Bradley, E., IPC Workshop, Minneapolis, MN, October 25, 1999.

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1. Thermount® is a registered trademark of E.I. du Pont de Nemours and Company.