Novel Dielectric Materials: Breaking the Gigahertz Barrier

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For many critical electronic applications, there is a need for dielectric systems that exhibit better electrical insulation performance than epoxies and other conventional materials. In the production of advanced telecommunications, high-speed electronic and microwave equipment as well as radomes and other products being developed today throughout the world, manufacturers rely on materials such as Teflon®, cyanate esters, and cyanate ester/epoxy blends to meet their performance requirements. However, these materials feature disadvantages that can make them costly and difficult to use as dielectrics in some of these demanding applications.

We have an active research program to develop novel new thermosetting polymers with low Dk/Df properties. This paper focuses on the testing of one of these materials as a base resin for PWB multilayers. This new system may also have applications outside the scope of this study.

1.0 Introduction

Organic polymers play a very important role in the manufacture of composite PWBs. Among the materials that have been used for building complex electronics are epoxies, phenolics, bismaleimides and cyanate esters. These polymers exhibit the required electrical insulation, thermal properties, chemical resistance and mechanical strength necessary for the applications.

Two of the most important measures of a polymer's ability to perform as a PWB resin system are the dielectric constant [Dk] and the dissipation factor [Df]. The dielectric constant determines the speed of the electronic signal in the PWB. The Df represents the dielectric loss of the signal in the circuit. Both values affect the size of the PWB and the signal quality. In addition, the size of the copper conductors and the insulation space on the PWB are affected by the Dk/Df values. Low Dk and Df characteristics will result in faster signal speeds with lower loss of power in the PWB. Therefore, resins with low Dk/Df properties support the production of small PWBs with close line/conductor spaces.

One of the Huntsman materials currently under study for building PWBs is a new benzoxazine. Benzoxazines as a product family are good candidates for complex electronics because they:

- ⇨ Are a non-halogen systems [no chlorine or bromine]
- ⇨ Have high glass transition values
- ⇨ Exhibit low moisture absorption
- ⇨ Feature flammability resistance that is better than epoxies

Although this class of products also has good electrical properties with low Dk and Df values, the Dk/Df properties are not stable at all frequencies. When these materials are tested at ≥1 GHz, their Dk/Df values increase substantially. As a result these systems are difficult to use for electronics that operate at higher frequencies

Recently, we developed a new experimental material with electrical properties that remain stable at frequencies in the gigahertz range.

2.0 General Benzoxazine Chemistries

The synthesis of benzoxazine compounds from phenols, formaldehyde and amines has been studied in detail by several groups[1-5].

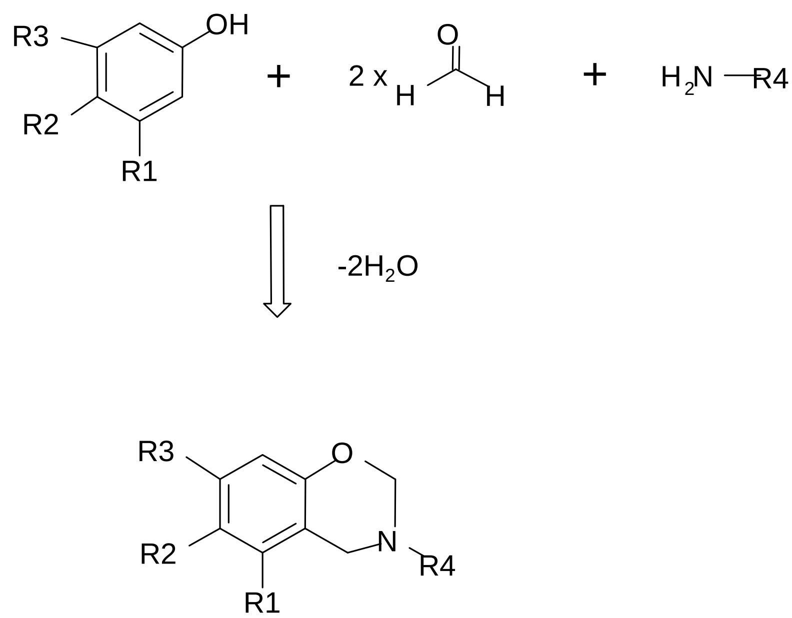

Figure 1. Synthesis of Benzoxazine

It is also recognized that these compounds, when heated, homopolymerize to form high molecular weight polymers. When multifunctional phenols and/or multifunctional amines are used, highly cross linked polymers are produced.

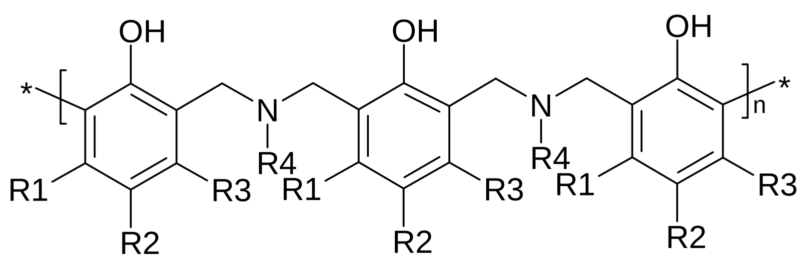

Figure 2. Homopolymerization of Benzoxazine

3.0 Experimental

In evaluating the new developmental candidate, electrical testing was performed on neat resin samples. This was done to provide a better understanding of the effect of the resin on the PWB because the electrical properties of laminates are dependent on ratio of fiberglass to resin. The new developmental candidate was formulated with dicyclopentadiene epoxy[7] [DCPD] for easy casting and fabrication of a copper clad laminate for the tests.

3.1 Sample Preparation

3.1.1 Neat Resin Sample Preparation

Neat resin castings of various resin systems were made for testing. The materials were melted, degassed and poured into a mold. The polymer was then cured using a cure cycle appropriate for the production of suitable castings.

3.1.2 Laminate Sample Preparation

Fiberglass laminate composites were made using a solvent impregnation process. Typically, the resin was dissolved in MEK along with suitable catalysts, and then coated onto 2116 fiberglass cloth. The solvent was then evaporated and B-staged. The prepreg with copper was then laminated under heat and pressure to produce a copper-clad laminate. These laminates were evaluated for their thermal and flammability properties.

3.2 Evaluation Tests

3.2.1 Dielectric Constant (Dk)/Dissipation Factor (Df.) Dk was measured using Hewlett Packard HP 4291 impedance analyzer at frequency range of 10 MHz to 1.5 GHz.

3.2.2 Glass Transition Temperature (Tg). Tg was measured with Differential Scanning Calorimetery (DSC) and Thermal Mechanical Analyzer (TMA) using procedures described in IPC-TM- 4101

3.2.3 Coefficient of Thermal Expansion (CTE). CTE was measured using TMA according to the IPC-TM-4101

3.2.4 Flammability Test. Flammability testing was conducted on the unclad glass-reinforced laminate as per UL 94 requirements

3.2.5 Decomposition: Decomposition was determined by using a thermogravimetric analyzer. Sample specimens were 10–20 mg analyzed in air with a heating rate of 10°C per minute.

3.3 Neat Resin Properties

Table 1 Neat Resin Electrical Properties in the Megahertz Range

Resin Type	DK Range	Df Range
Brominated Bisphenol A Epoxy	3.5 – 3.6	0.0200 – 0.0250
Dicyclopentadiene Cyanate Ester	2.70 – 2.80	0.0040 – 0.0050
Bisphenol A Benzoxazine	3.00 – 3.15	0.0060 – 0.0100
Dicyclopentadiene Benzoxazine	2.80 – 2.85	0.0040 –0.0060
Bisphenol F Benzoxazine	3.40 – 3.60	0.0070 – 0.0090
Phenolphthalein Benzoxazine	3.20 – 3.50	0.0080 – 0.0120
Development candidate /DCPD epoxy	2.50 - 2.70	0.0001 – 0.0033

1. HP 4291A impedance analyzer
2. Test range 10 MHz – 1.5 GHz.
3. Neat resin sample thickness 2.0mm – 2.5 mm
4. Brominated Bisphenol A epoxy made from LZ8001.
5. Development candidate/DCPD epoxy is @ 50:50 ratio.

Test results show that the development candidate has dielectric properties better than epoxy, exhibiting performance close to cyanate esters. The table below shows the property changes in the electrical values when they are tested at higher frequencies.

Table 2 Neat Resin Electrical Properties in the Higher Gigahertz Range

Resin Type	DK Range	Df Range
Brominated Bisphenol A Epoxy	3.5 – 3.7	0.0400 – 0.0750
Dicyclopentadiene Cyanate Ester	2.8 – 3.4	0.0040 – 0.0080
Bisphenol A Benzoxazine	3.1 – 3.6	0.0060 – 0.0300
Dicyclopentadiene Benzoxazine	2.8 – 3.6	0.0020 – 0.0080
Bisphenol F Benzoxazine	3.3 – 3.9	0.0140 – 0.0480
Phenolphthalein Benzoxazine	3.3 – 3.7	0.0090 – 0.0390
Developmental candidate /DCPD epoxy	2.5 - 2.7	0.0010 – 0.0050

1. Aligent E8364B network analyzer
2. Test range 10 GHz – 25 GHz.
3. Neat resin samples thickness 2.0mm – 2.5 mm

The charts below show the electrical values of the new developmental candidate material as compared to Teflon® and cyanate ester. The results here show that the new developmental candidate is more stable in the frequency range than the cyanate ester.

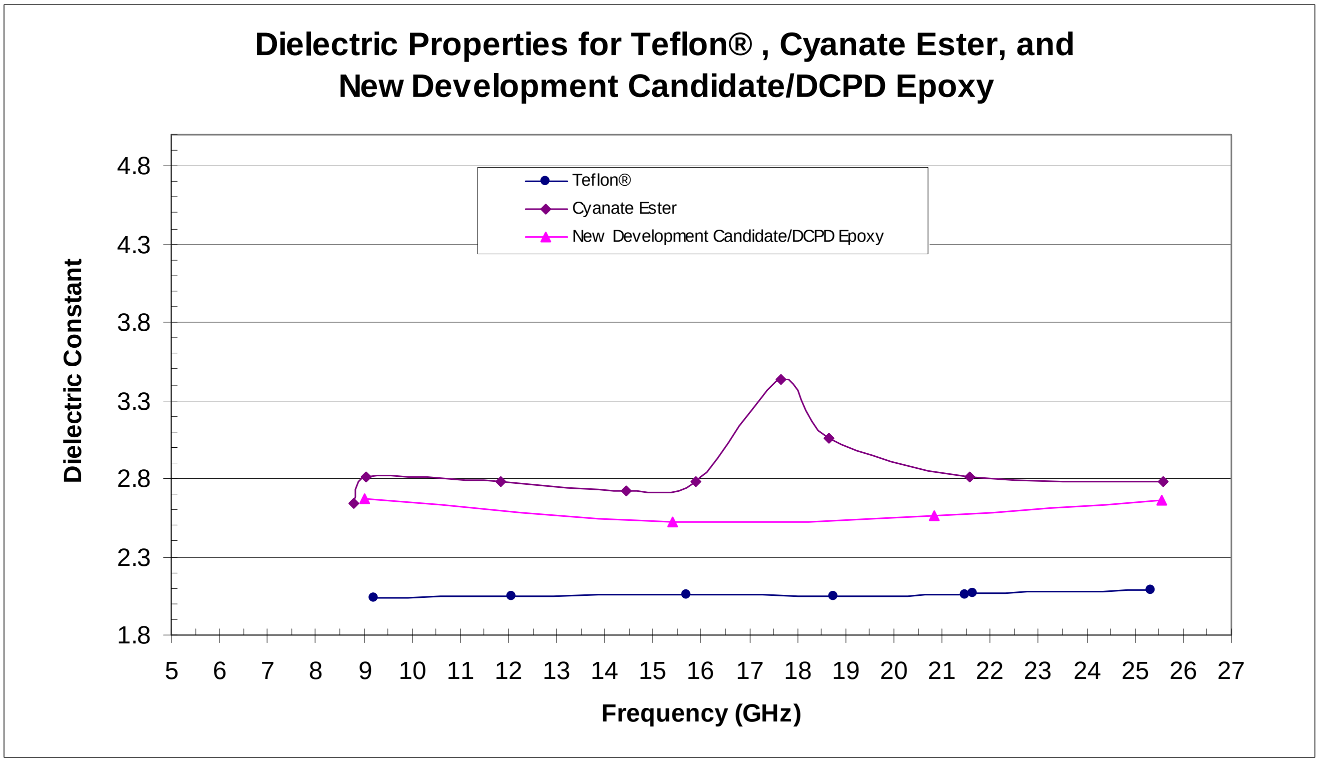

Figure 3

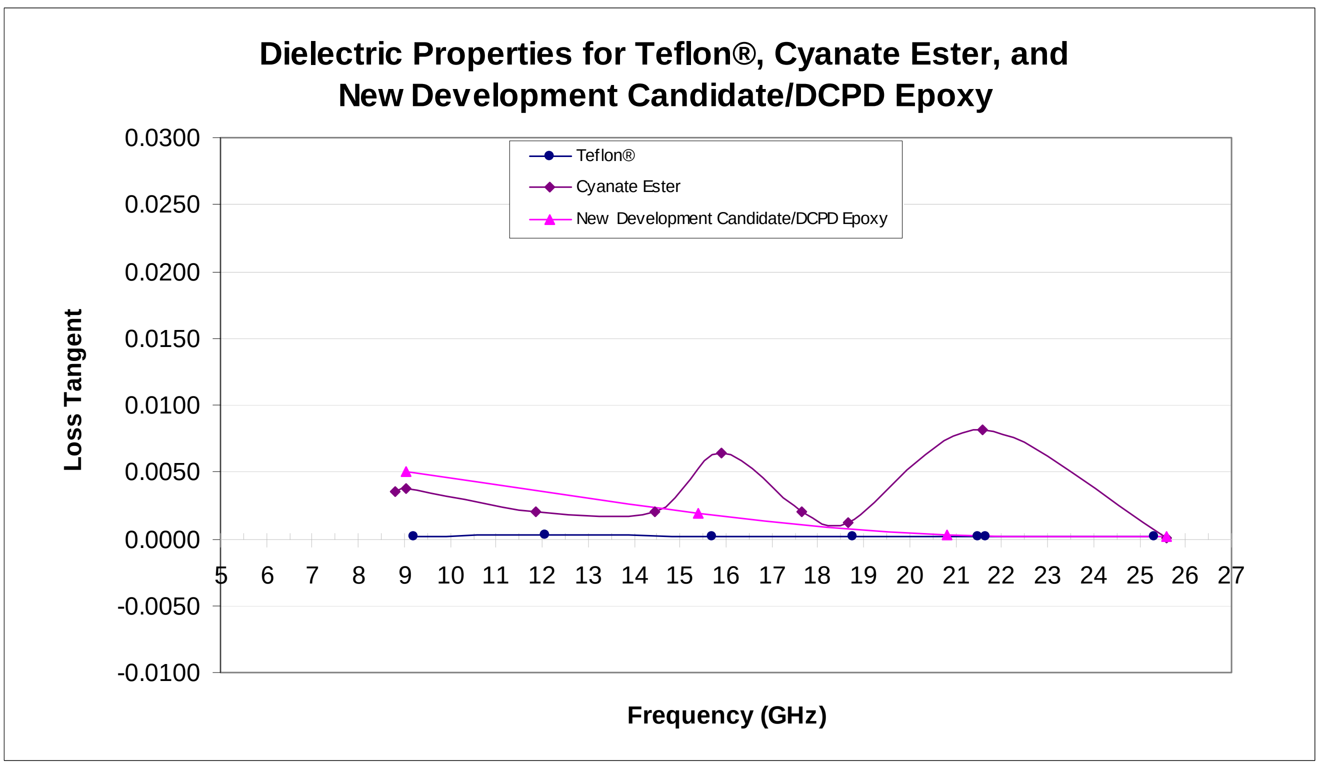

Figure 4

3.4 Copper-clad Laminate

Preliminary laminate resin properties with the development candidate/DCPD epoxy system are shown in the table below. The resin material was solvated in MEK and then prepregged with fiberglass. The fiberglass prepreg was laminated with copper foil and cured.

Laminate Properties

Property	Results
Glass Transition Temperatures DSC TMA DMA (tan delta)	 144.60 °C 130.70 °C 167.40 °C
CTE $_{60°C\ to\ 80°C}$, TMA	42.46 µm/°C
Decomposition Onset, TGA	350.34 °C
UL94 Flammability Testing Rating Total burn time, secs.	 V1 180 – 240 seconds [typical]

Notes:
1. 12 plies 2116 laminate.
2. Cured @ 400°F for 2 hours.
3. Resin content 48% – 50%
4. IPC 4101 test methods.
5. Electrical testing was done using the HP4291A Impedance Analyzer and the Aligent E8364B network analyzer.

Conclusion

The low Dk/Df testing is an ongoing project, with a goal of developing materials for PWB applications as well as for other electronic applications. The preliminary resin system described here shows the promise that these new systems can be developed for low Dk/Df PWB applications. The primary advantages of this development candidate/epoxy system are that it has good electrical properties and is a non-halogen- based material.

The focus of future work will be:

- ⇨ Improving flammability to UL 94 V-0 requirements
- ⇨ Increasing the Tg
- ⇨ Demonstrating lead-free performance
- ⇨ Evaluating electrical properties under varied environmental conditions. [temperature, humidity, chemical resistance]

References

1.A.C. Cope and F.W. Holly J Amer. Chem. Soc. 66 1875 (1944)
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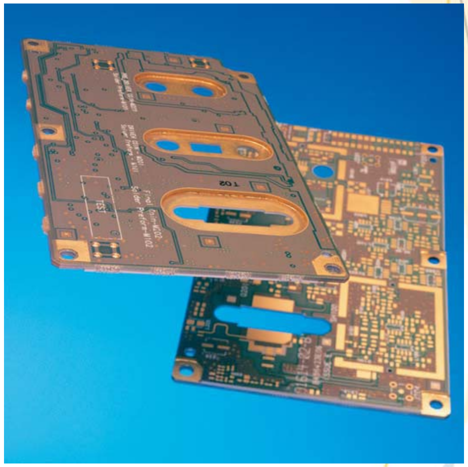
3. W.J. Burke and E.L. Montesen, J Org Chem., 29 909 (1964)
4. G, Reiss, J.M. Schwob, G Guth, M. Roche and B. Laude, in Advances in Polymer Synthesis, B.M. Gulberston and J.E. McGrath, Eds., Plenum, New York, 1986
5.X. Ning and H Ishida, J of Polymer Science B, 32 921-927 (1994)
6. Dicyclopentadiene epoxy used was Huntsman Tactix 756 ®.
7. Dicyclopentadiene cyanate used was Arocy® 782.

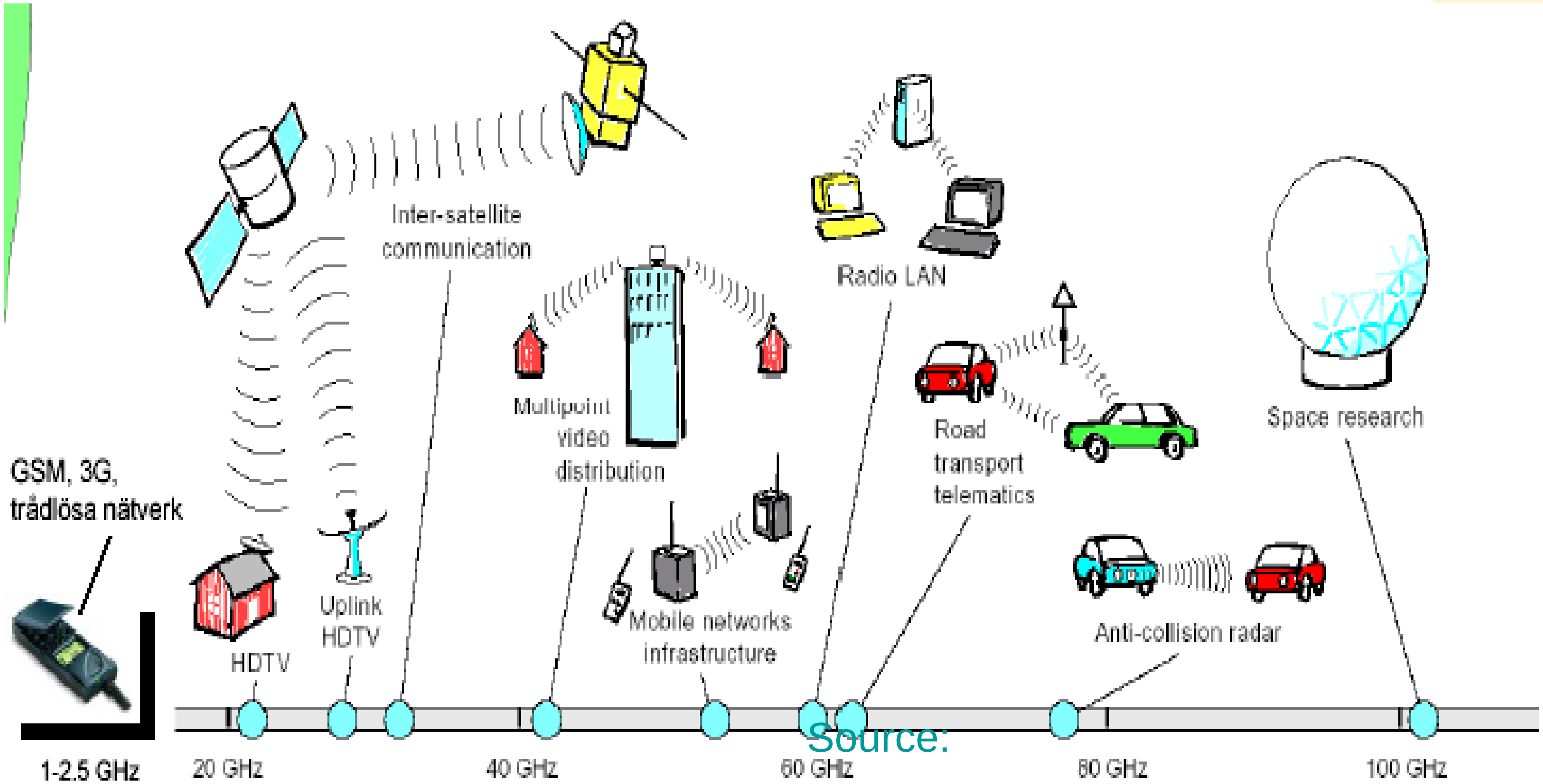
Novel Dielectric Materials Breaking the Gigahertz Barrier



Roger Tietze
Huntsman

- Introduction
- Market Needs
- Current Technology
- Huntsman Development Program
- Testing
- Conclusion

High Frequency Applications



Opportunity for laminate resins with low Dk/Df.

Resin based laminates & dielectrics needed for high speed aplications at higher frequencies

Material Requirement: Low Dk & Low loss factor (High speed materials)

Fequency GHz

Existing
Technology (epoxy)

Target &Potential for new Technology

< 1 | 1-5 | 5-10 | 24 | 77 | 100 GHz

ex. Telecom base stations, wireless, digital backplane

ex.Telematics / Radar (auto)

Material

FR 4 (Epoxy)

Teflon®-Ceramic-Epoxy-PPO

LTCC (Low Temp Co-fired Ceramic

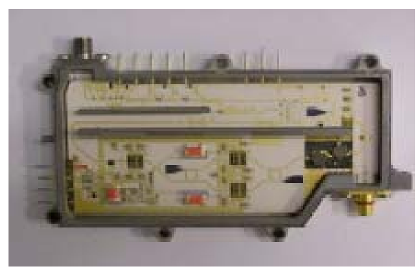
(Polyimide)

Cyante esters

or very pure Teflon qualitity

Process

”High speed”
Substrates, specially on top
layer.



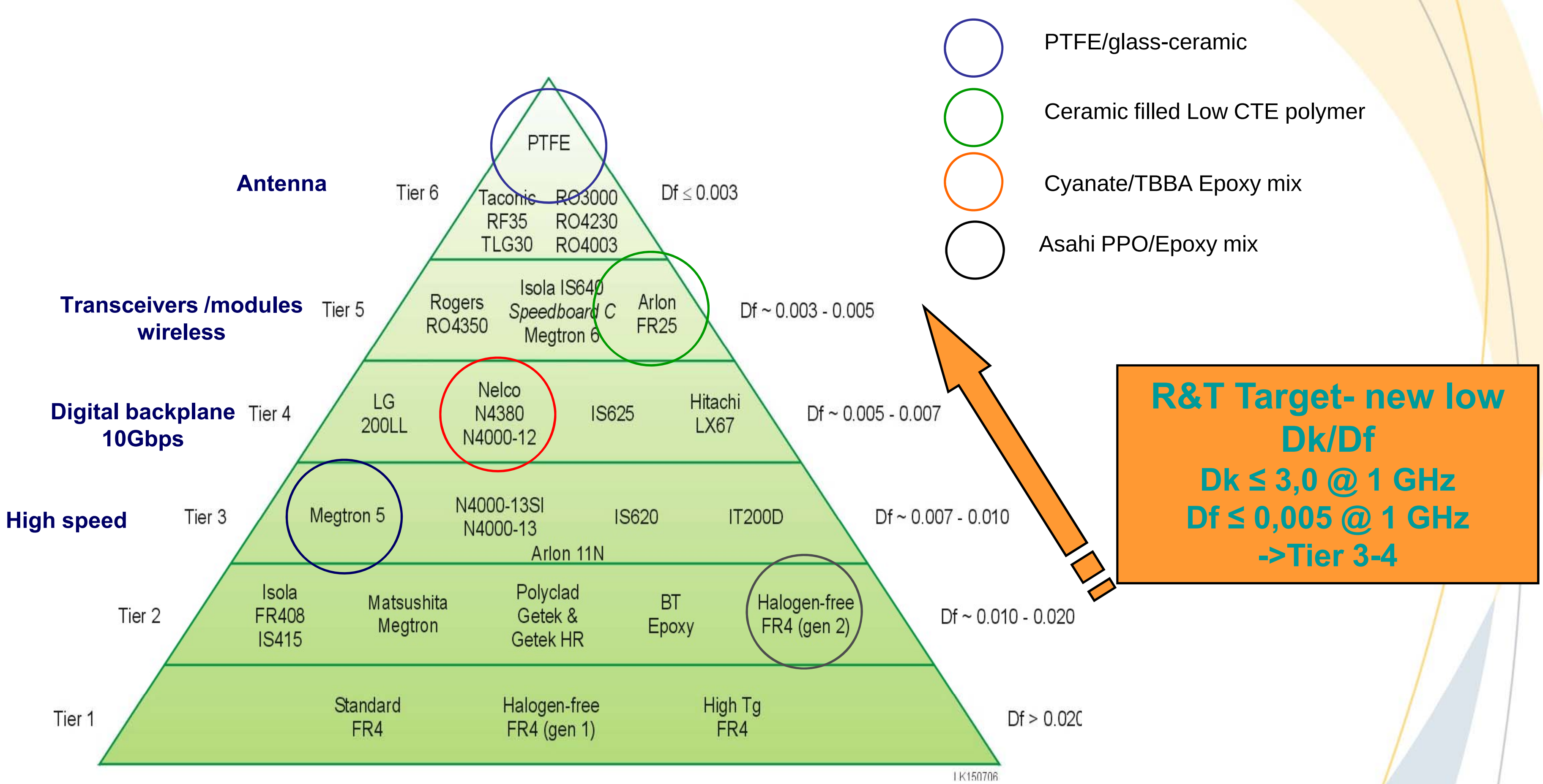
Thin film Ceramic
Polymer Thick film
Co-fired at ~ 900 C
With or w/o
Embedded Passives
integration.

Standard
”PCB process”

Special
”PCB process”

LTCC process / Polymer thick film etc.

Prepreg Material Pyramid



Source: BPA

Market Needs

- Market is looking for laminates with **stable** Dk/Df in high frequency range, preferable over a wide frequency e.g 1MHz-10GHz
- Benzoxazine's are fulfilling requirements up to Tier 2, but so far not stable enough in high frequencies,1 GHz-10 GHz, range.
- Teflon® and hybrid materials (teflon, teflon®/ceramic, PPO, cyanate esters) are very expensive and /or have poor mechanical properties .The materials require special treatment & processing in PWB manufacturing.
- Product should be easy to process (as an "FR-4 process")

Base Resin Chemistry Summary

- Epoxy Systems
  - Proven technology
  - Electrical properties do not meet requirements Tier 3-6
  - Economical
- Benzoxazines
  - Very good properties [thermal, mechanical, and chemical]
  - Electrical properties below 1 GHz very good. Above 1 Ghz the DK/Df increase substantially
  - Economical
- Bismaleimides/ Polyimides
  - Excellent overall high temperature performance properties
  - Electrical properties better than epoxy
  - Economically competitive

Electrical properties do not meet requirements Tier 3-6

- Cyanate esters
  - Excellent electrical properties, and do meet requirements for upper tiers
  - Good thermal properties
  - Very high cost

Huntsman Development Program

Key Goals

- Steady state electrical properties [thermal, moisture, etc.]
- Flammability resistance
- Green technology [ie: nonhalogen]
- Reasonable processing temperatures [FR4 processing]
- Good thermal performance [Lead free requirements]
- Economical

Huntsman Technical Approach

- Benzoxazines Chemistry
  – Proven non-halogen technology
  – Compatible processing with epoxy
  – Desirable high performance properties
  – Potentially cost effective

- RD2001-78 Chemistry
  – Bismaleimide cured system
  – Excellent electrical properties
  – High temperature processing required
  – Build on basic chemistry to improve processing

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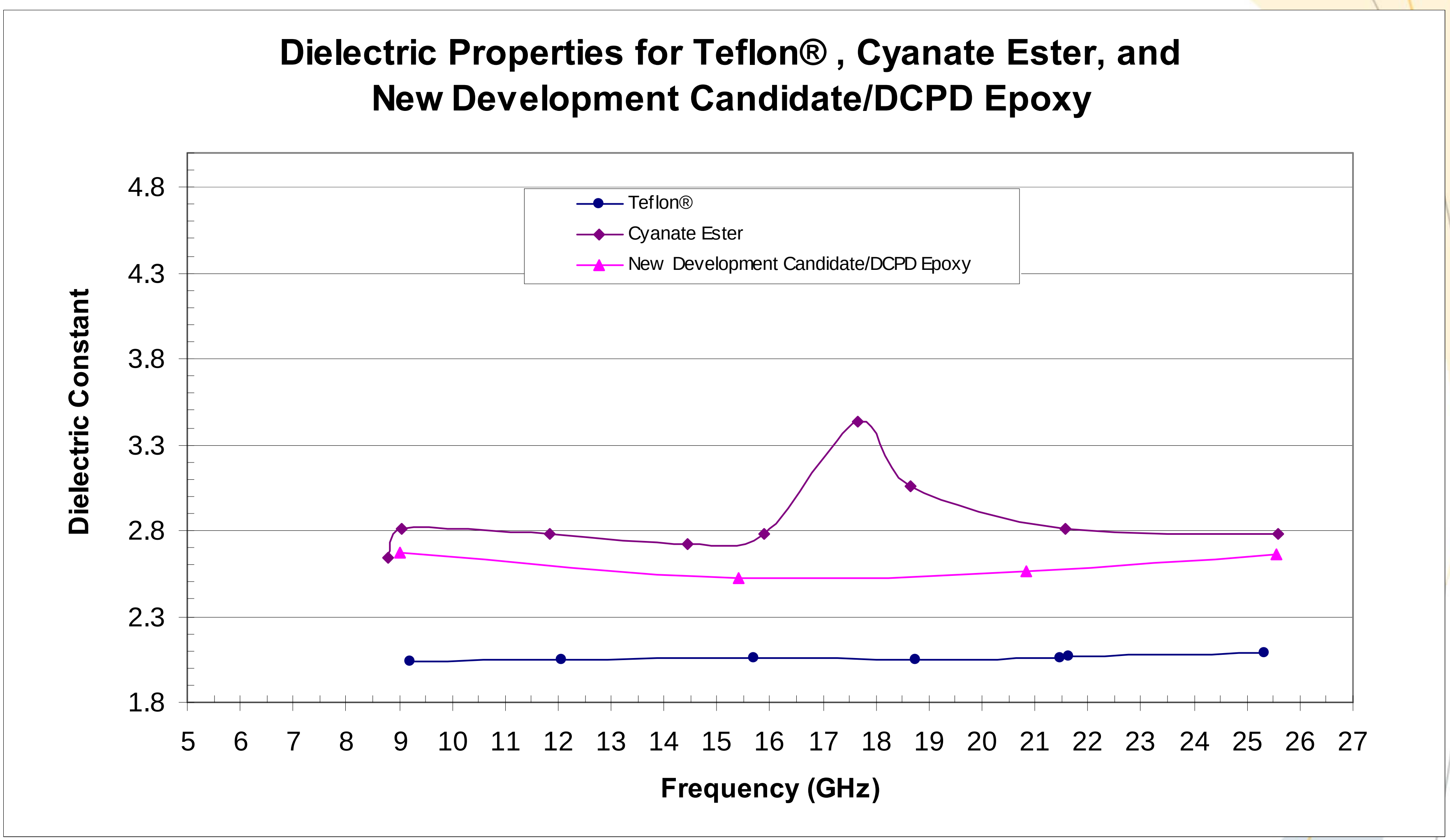
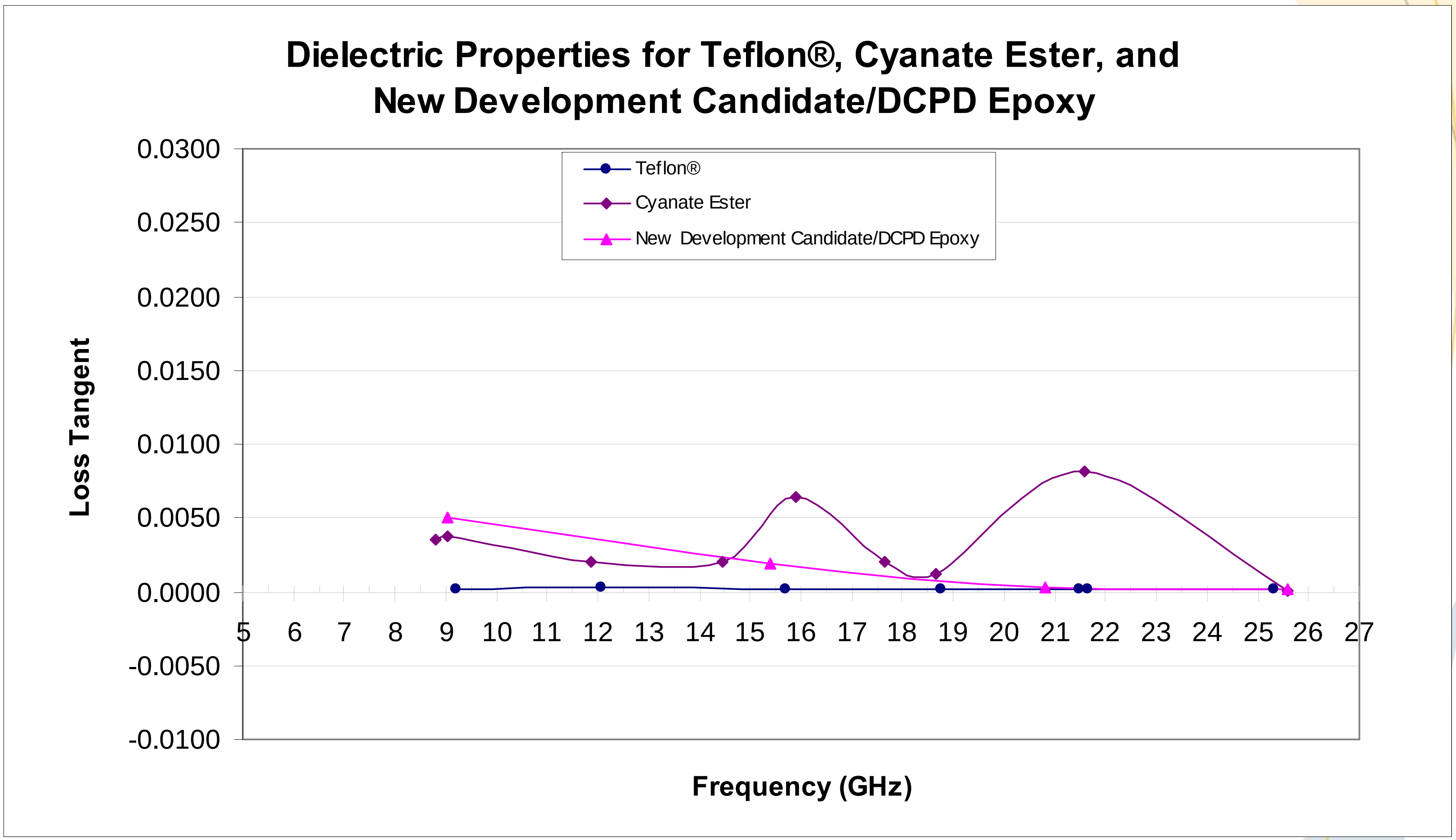


Dielectric Properties for Teflon® , Cyanate Ester, and
New Development Candidate/DCPD Epoxy
Teflon®
Cyanate Ester
New Development Candidate/DCPD Epoxy
Dielectric Constant
4.8
4.3
3.8
3.3
2.8
2.3
1.8
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
Frequency (GHz)



Dielectric Properties for Teflon®, Cyanate Ester, and
New Development Candidate/DCPD Epoxy
Teflon®
Cyanate Ester
New Development Candidate/DCPD Epoxy
Loss Tangent
0.0300
0.0250
0.0200
0.0150
0.0100
0.0050
0.0000
-0.0050
-0.0100
5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27
Frequency (GHz)

PWB Testing

Development Candidate/DCPD Epoxy

- The resin material was solvated in MEK
- Prepregged with fiberglass.
- The fiberglass prepreg was laminated with copper foil and cured.
- Laminate was then tested

Laminate Testing

Property	Results
Glass Transition Temperatures DSC TMA DMA (tan delta)	144.60 °C 130.70 °C 167.40 ° C
CTE $_{60°C\ to\ 80°C}$, TMA	42.46 µm/°C
Decomposition Onset, TGA	350.34 °C
Dk @ 10 MHz - 1 GHz Df @ 10 MHz - 1 GHz Dk @ 10 GHz - 20 GHz Df @ 10 GHz - 20 GHz	3.3 – 3.5 0.002 – 0.006 3.3 - 4.1 0.002 – 0.012
UL94 Flammability Testing Rating Total burn time, secs.	V1 180 – 240 seconds [typical]

Notes:
1. 12 plies 2116 laminate.
2. Cured @ 400° F for 2 hours.
3. Resin content 48% – 50%
4. IPC 4101 test methods.
5. Electrical testing was done using the HP 4291A impedance analyzer and the Aligent E8364B network analyzer

Huntsman Test Equipment

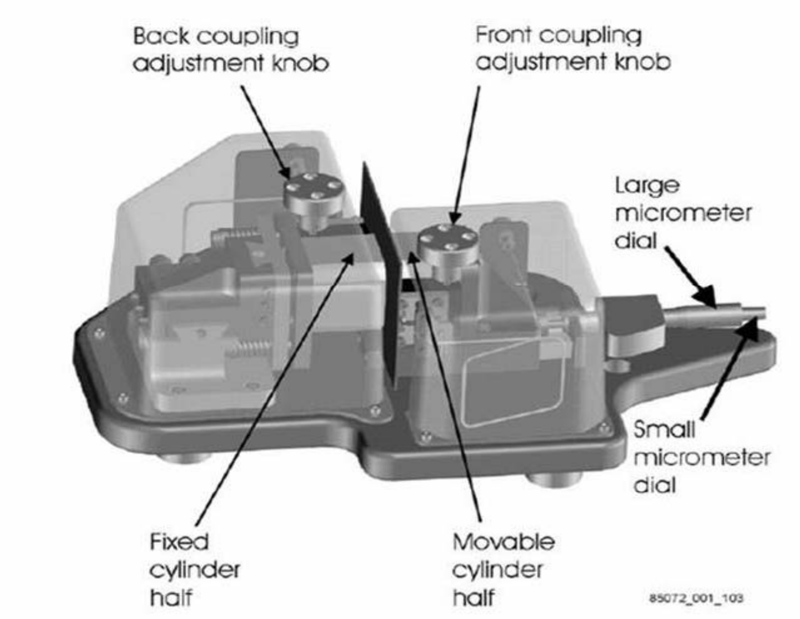
- Network Analyzer up to 50GHz
- Multiple frequency analysis by Split Cylinder resonator
- Split post fixtures @ 2, 5, 10, 15, and 20 GHz
- Teflon is used as a control
- Dicyclopentadiene Cyanate ester neat resin is used as a control. Specimens will be made as neat resin casting and laminate specimens will also be made.

Network analyzer E8364B with option 300
Split cylinder resonator (10 GHz)

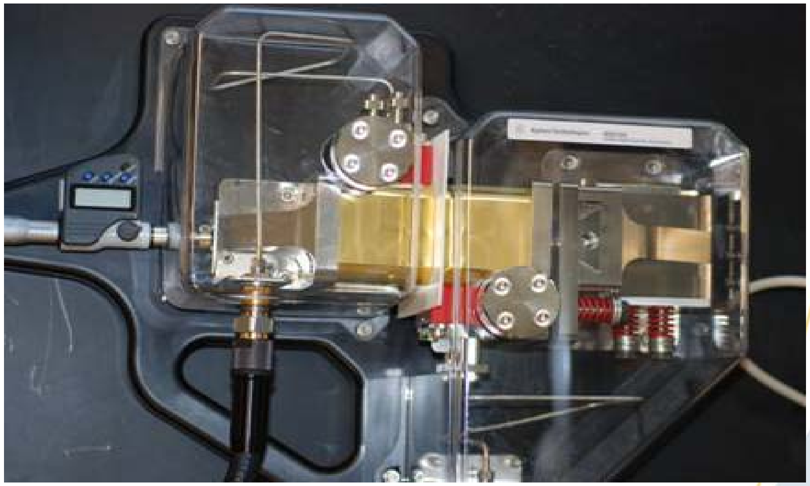
Split Cylinder Resonator: 10 GHz

Split Cylinder Resonator

Front view



Top view



Summary

- Developing materials for PWB applications as well as for other electronic applications.
- The preliminary work described here shows the promise that new materials can be developed for low Dk/Df PWB applications.
- The primary advantages of this development candidate/epoxy system are that it has good electrical properties and is a non-halogen- based material.
- The focus of future Huntsman work will be:
  - Improving flammability to UL 94 V-0 requirements
  - Increasing the Tg
  - Demonstrating lead-free performance
  - Evaluating electrical properties under varied environmental conditions. [temperature, humidity, chemical resistance]

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