#### Polyphenylene Ether Macromonomer. Viii. Low Z-Axis Cte, Low D<sub>f</sub> Epoxy Laminates

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#### Abstract

Properties of printed circuit board laminates are a function of the type and levels of its components. Endeavors to a balance various performance criteria involve balancing the types and amounts of materials that can have similar or opposite effects on key properties. This paper explores the combined use of silica with use of silica and PPE macromonomer in optimizing properties of epoxy-based laminates. Silica exhibits low dielectric properties. However, particulate fillers can lower the toughness of composites. PPE macromonomer has been shown to be very effective in enhancing properties of epoxy-based laminates. In particular, PPE macromer increased the toughness and improved the dielectric properties of epoxy-based laminates. Hence, the combination of PPE macromer and silica filler suggests a way to expand the performance window of epoxy-based laminates. Structure property evaluations were used to quantify the effects epoxy/silica, epoxy/PPE, and epoxy/PPE/silica on dielectric properties, CTE, toughness, and flexural properties. Types of silicas evaluated included ground, fused, platy, and diatomaceous earth. The results showed that using the macromoners in conjunction with silica give performance enhancements over epoxy-silica, or epoxy-PPE alone. Epoxy-based laminates were made which exhibited low Z-axis CTE and low loss tangent.

#### Introduction

Complex microelectronics devices place high demands on dielectric materials. The electronics industry is propelled by constant technological changes, which have brought improved, innovative products to the marketplace. [1,2] Dielectric materials play a critical role in the advancement of the microelectronics industry. The continuous progression toward portable, high frequency microelectronic systems places high desideratum on material performance, notably low dielectric constants ( $D_k$ ), low loss tangent ( $D_f$ ), low coefficient of thermal expansion (CTE), low moisture uptake, and good thermal stability.

Some of the properties of a laminate that have been identified for improved balance of properties are discussed in the following paragraph. Dielectric constant,  $D_k$ , relates to signal speed. A low  $D_k$  implies higher signal propagation velocity. The loss tangent,  $D_f$ , is a measure of how much of the power of a signal is lost as it passes along a circuit on a dielectric material. A low  $D_f$  implies low signal loss. The CTE is a thermo-mechanical property of materials. It is the tendency of a material to expand when heated. Organic materials such as resins have a higher CTE than inorganic materials such as glass fiber and metals. The glass cloth lies in the plane of the laminate (the X and Y direction). Hence, the CTE in the X and Y direction is generally very low. However, the CTE for out-of-plane expansion (the Z-direction) can be much higher. The plated through holes in a laminate are in the Z-direction. The Z-direction expansion will cause shear stresses within the solder joint that mounts the device on the board. Hence, low CTE in the Z-direction is important. Water has much higher dielectric properties than the components used to make laminates. Thus, lower water absorption would result in more stable dielectric properties and allow for shorter baking times to remove water for secondary operations, which can result in economic benefits.

These trends in the microelectronics industry have placed new challenges on epoxy-based laminates. The aim of this paper is not a comprehensive account of the physical properties but rather a discourse of raw materials with an indication of the ways in which "materials engineering" can be used to design and optimize materials with enhanced performance.

The optimization is focused on judicious formulating with epoxy, PPE macromonomer, glass fiber, and silica filler. Epoxy resins are the workhorses of the electronic industry. There are a very wide variety of epoxy resins. They have good dielectric properties, but needs to be lower for high-speed digital applications. Its CTE is high compared to inorganic materials. [3]

PPE macromonomer, PPE-M, is a low molecular weight telechelic version of PPE, an engineering thermoplastic. The macromonomer retains most of the key features of PPE including a very high glass transition temperature  $(T_g)$ , outstanding dielectric properties over a wide temperature range, and very low moisture absorption. [4-7] Like epoxy resins, the CTE is high. The utility of PPE macromonomers in enhancing the performance of thermoset resins has been demonstrated previously. [8-13]

Several types of glass fibers are available. [14, 15] They all feature high modulus and low CTE. E-glass, aluminum/boron/silicates glass, is very common and is used widely in laminates and composites. Indeed, E-glass is used

extensively in copper clad laminates. It has a much higher  $D_k$  than resins commonly used. S-glass is a high strength, high modulus fiber that is used primarily in the structural and composites industries. It was has been evaluated in laminates. Its  $D_k$  is approximately 15% lower than E-glass and its cost higher. Quartz, or fused silica glass, have low  $D_k$  and  $D_f$ . However, quartz glass is expense and brittle. Handling and processing are described as poorer than E- or S-glass. The focus of this paper is on the challenge of using E-glass and lowering  $D_k$ ,  $D_f$ , and CTE of the epoxy-based laminates.

Mineral fillers have long been used to modify the properties of polymers. An important function of reinforcing fillers and fibers in plastics is the reduction of the thermal expansion. Silica, silicon dioxide, is the most abundant mineral on earth. Several types of silica are used as fillers. Quartz, a natural grade of crystalline silica, is resistant to heat and chemicals. Fused quartz is made by melting (fusing) crystalline quartz and refined such that an amorphous substance is formed. Diatomaceous earth (DE), diatomaceous silica, is a naturally occurring mineral derived from microscopic, fossilized remains of marine diatoms. In general, silicas have very low CTE, high thermal conductivity, and very good electrical properties. However, particulate fillers can act as a defect in the polymer matrix and lower the toughness of composites.

#### Materials

Silica: Four different types of silica were evaluated. A high purity, high quality natural ground crystalline silica was supplied by U. S. Silica under the Min-U-Sil<sup>™</sup> 5 trademark. Another ground silica, which was listed as having plately particle shape, was supplied by Malvern Minerals Co. under the Novacite<sup>™</sup> L207 trademark. Spherical fused silica was supplied by Denki Kagaku Kougyo Kabushiki Kaisya under the Denka Fused Silica FB-3 designation. C:\eu\ProductDetail.asp?PID=497A calcined diatomaceous earth was supplied by Imerys Minerals Ltd. under the Celite Super Fine SuperFloss<sup>™</sup> trademark. This grade was chosen because of its high SiO<sub>2</sub> content. In this paper, the levels of silica studied were 10, 25, and 40 phr (parts per hundred resin). Acronyms and a comparison of some properties are shown in Table 1. The chemical purity was from the manufacturers. The particle size analysis of the silica samples was determined using a Mastersizer S instrument by the authors. Samples were suspended in water, using an ultrasonic probe. Both D(4.3)[the equivalent volume mean diameter or the De Broncker mean diameter] and D(3.2) [the equivalent surface area mean diameter or the Sauter mean diameter] are similar. However, the spherical silica has a much narrower particle size distribution.

Designation	SPH	PLA	GRD	DE
Shape	Spherical	Platev	Ground	Diatoms
Density, g/cc	2.2	2.65	2.65	2.3
Particle size				
D(4,3), µm	4.06	3.46	2.38	5.79
D(3,2), µm	2.71	1.12	1.01	2.06
D(v, 0.1), μm	1.44	0.45	0.4	1.05
D(v, 0.5), µm	3.25	2.56	2.03	4.61
D(v, 0.9), µm	7.75	7.55	4.8	11.78
Composition, %				
SiO <sub>2</sub>	99.7	99.49	98.5	89.6
$Al_2O_3$	-	0.102	1.0	4.0
CaO	-	0.014	0.04	0.5
MgO	-	0.021	0.02	-
$Na_2O + K_2O$	< 0.01	-	0.06	-
TiO <sub>2</sub>	-	0.015	0.02	-
$Fe_2O_3$	< 0.01	0.039	0.09	-

#### Table 1. Comparisons of silica fillers

PPE macromonomer: The PPE-M telechelic oligomer is available from Sabic Innovative Plastics under the developmental designation Noryl® MX90 (commercial designation Noryl® SA90). This hydroxyl-terminated oligomer is designed for use with epoxy resins and cyanate ester resins. [8, 9] In this paper, the levels of PPE-M studied were 30, and 50wt%. The structure of PPE-M is depicted in Figure 1.



Figure 1. Structure of PPE-M

Epoxy resins: The diglycidyl ether of bisphenol-A will be designated by the DGEBPA acronym or simply epoxy in this paper. It was supplied by Dow Chemical Company under the D.E.R. <sup>™</sup> 332 tradename. It was chosen for its low epoxy equivalent weight (EEW). Brominated bisphenol-A diglycidyl ether was supplied by Dow Chemical Company under the D.E.R. <sup>™</sup> 560 trademark. In this paper it will be designated Br epoxy. The catalyst used to cure the epoxy resins was 1.5phr 2-ethyl-4-methyl imidazole (2,4-EMI).

The glass cloth used to make laminates was 7628-E glass cloth with a 642 finish (from BGF Industries).

#### **Experimental**

The examination of the performance of castings provides a unique window to observe the quantifiable effect of various components used to make the epoxy matrix. Hence, castings were prepared to study the effect of silica and PPE-M incorporated into the epoxy network. The PPE-M levels were 0, 30, and 50wt% based on total resin (PPE-M and epoxy). The levels of the four types of silica were 10, 25, and 40 phr. Castings were prepared by dispersing the silica in 2-butanone (MEK) using a high-speed mixer. The PPE-M was dissolved in the silica/MEK mixture with stirring and warming to 60-70°C. Then the epoxy resin was added and dissolved. Catalyst was added and the solvent removed. The mixture was transferred to a compression mold and cured up to 230°C. A plaque of the cured composition was removed and cut into test parts using a tile cutting saw with a diamond-cutting blade.

#### **Results and Discussion**

The use of particulate fillers in plastics can have various consequences on performance. [19] In general, the density, strength, modulus, and impact strength can increase. On the other hand, fillers can increase a material's sensitivity to notches and cracks. [20, 21] The fillers can introduce imperfections in the polymer matrix. In an unnotched specimen the deformation tends to take place throughout the length of the specimen. In a notched specimen, most of the deformation takes place in the neighborhood of the tip of the notch. The main reason for this is that notches are stress concentrators resulting in notched impact strengths lower than that of unnotched specimens. The important implication for electronic applications is toughness to survive drilling holes in the laminate.

The effect of silica and PPE-M on the density appears in Figure 2. The density increases with increasing levels of silica. On the other hand, the density decreases with increasing levels of PPE-M. Castings containing SPH and DE have slightly lower densities, which is attributed to the lower densities of these silicas.



Figure 2. Effect of silica and PPE-M on density

Flexural modulus and strength increased with increasing levels of silica. The amount of silica appears to be more important than the type of silicas used in this study. However, the DE specimens consistently exhibited slightly lower flexural properties. For epoxy and epoxy/silica castings with 10, 25, and 40phr silica, the average increase in modulus was 21, 51, and 81%, respectively. Compared to epoxy, 30 and 50wt% PPE-M decreased the modulus of epoxy/PPE-M 12 and 21%, respectively. For PPE-M/epoxy/silica castings, there was a decrease in modulus compared to epoxy only castings. With 30wt% PPE-M and 10, 25, and 40phr silica the flexural modulus decreased 2, 18, and 36%, respectively. With 50wt% PPE-M and 10phr silica the average flexural modulus decreased 11%. However, there was an increase in flexural modulus of 2, and 13% with 50wt% PPE-M and 25 and 40phr silica, respectively. The data are shown in Figure 3.



Figure 3. Effect of silica and PPE-M on flexural modulus

The flexural strength for epoxy and epoxy/silica castings with 10, 25, and 40phr silica showed an average increase in strength of 9, 24, and 40%, respectively. The PPE-M/epoxy/silica castings 30wt% PPE-M exhibited -2, 8, and 21% changes, respectively. With 50wt% PPE-M the castings exhibited -10, -3, and 6% changes, respectively. The data appears in Figure 4.



Figure 4. Effect of silica and PPE-M on flexural strength

Methods for measuring toughness include pendulum impact strength or Izod impact strength (high-speed crack propagation), and fracture toughness (low speed of crack growth). Because of the large number of samples in this study, pendulum impact was used to study the toughness. Both notched and unnotched specimens were evaluated. In general, notched samples exhibit lower values than the unnotched specimens. The main reason behind this behavior was that notches act as stress concentrators, which lead to a decrease in the impact strength.[22] The stress concentration is highest at the tips of the notch. Hence, most of the deformation takes place in the neighborhood of the notch tip in notched specimens. Whereas, unnotched specimens tend to have deformations take place throughout the length of the specimen. In addition, the sensitivity to notches is affected by the fact that the fracture process involves both crack initiation and propagation. In notched specimens, an apparent crack is already initiated, so the energy absorbed is dependent primarily on the energy to propagate the crack. However, in unnotched specimens, the energy to initiate the crack is added onto that required for its propagation.

The effect of the type and amount of silica on notched impact strength appears in Figure 5. The impact strength decreases with increasing levels of silica. The amount of silica appears to be more important than the type of silicas used in this study. On average 10, 25, and 40phr silica decreased the notched impact strength 39, 64, and 76%, respectively, versus the epoxy by itself. The PPE-M minimized or overcame the adverse effects of the silica on impact strength. For example, at 50wt% PPE-M and 10 and 25phr silica the notched impact strength increased 37 and 4%, respectively. The 75% decrease in impact strength from 40phr silica, was minimized to a 20% decrease with 50wt% PPE-M.



Figure 5. Effect of silica and PPE-M on notched impact strength

Pendulum impact on unnotched samples showed an increase in impact strength with increasing levels of silica. In general, the amount of silica appears to be more important than the type of silicas used in this study. However, the DE specimens consistently exhibited slightly lower impact strengths. The properties appear in Figure 6. Compared to the epoxy matrix, epoxy/silica with 10, 25, and 40phr silica exhibited average increases in unnotched impact strength of 34, 86, and 120%, respectively. In epoxy/PPE-M, 30 and 50wt% PPE-M increased the unnotched impact strength by about 127 and 311%, respectively. The combined effect of silica and PPE-M resulted in significant increases in impact strength from 127 to 540% over epoxy by itself.



Figure 6. Effect of silica and PPE-M on impact strength

A correlation between pendulum impact strength (unnotched) and flexural modulus and strength appears in Figures 7 and 8. The correlations coefficients ( $R^2$ ) were between 0.978 and 0.991. These results suggest that the increase rigidity and strength are in part responsible for the increased impact strength of these materials.



Figure 7. Impact strength versus flexural modulus



Figure 8. Impact strength versus flexural strength

The effect of silica and PPE-M on  $D_k$  @ 1 GHz appears in Figure 9. As the silica levels increased there is a slight increase in  $D_k$ . Indeed,  $D_k$  increased an average of about 2, 4, and 6% with 10, 25, and 40phr silica, respectively. The spherical silica exhibited a lower increase in  $D_k$  than the other silicas. The PPE-M decreased the  $D_k$ . The average decrease with 30 and 50wt% PPE-M was 3 and 5%, respectively.



Figure 9. Dielectric constant versus silica and PPE-M

The loss tangent @ 1 GHz decreased with increasing levels of silica and PPE-M as shown in Figure 10. In epoxy/silica, 10, 25, and 40phr silica, decreased  $D_f$  an average of 5, 11, and 17%, respectively. The spherical silica was more effective in lowering  $D_f$  than the other silicas. With 30 and 50% PPE-M in epoxy/PPE-M  $D_f$  decreased 24 and 38%, respectively. Over the compositional range studied, the combination of silica and PPE-M gave reductions in  $D_f$  up to 46%.



Figure 10. Loss tangent versus silica and PPE-M

CTEs of dielectric materials gives an indication of the relative strain on a plated through holes on laminates at process temperatures such as soldering. In general, organic materials have much higher CTEs than inorganic materials. A key parameter in measuring CTE of polymers is the  $T_g$  of the material. In general, the CTE above the  $T_g$  of thermoset resins is much greater than the CTE below the Tg. The CTE below the  $T_g$  does not give a complete indicator of the expansion that can be expected at soldering temperatures. Lead-free solder temperatures are about 290°C. Hence, the total expansion over the range from 0 to 290°C is important.

A unique feature of epoxy/PPE-M resins is that the PPE-M gives an increase in  $T_g$  and a slight increase in CTE below and above the  $T_g$ . However, the overall CTE over the range from 0 to 290°C is decreased. A summary of CTEs for epoxy/PPE-M appears in Table 2.

PPE-M Wt%	$T_g$ °C	CTE 0°C- <i>T<sub>g</sub></i> ppm/°C	CTE <i>T<sub>g</sub></i> -290°C ppm/°C	CTE 0-290°C ppm/°C
0	133	55.76	185.29	121.08
30	155	57.12	195.40	116.57
50	167	58.10	201.60	113.96

Table 2. Effect of PPE-M on CTE of DGEBPA

Interestingly, even though there is a slight increase in CTE with the use of PPE-M, the CTE from 0 to 290°C is decreased. This phenomenon is related to the increase in  $T_g$  from the PPE-M. The relationship between increased  $T_g$  and lower overall CTE is shown graphically in Figure 11 for epoxy with 0 and 50wt% PPE-M. With 50% PPE-M the  $T_g$  is higher and hence there is a greater amount of the CTE below the  $T_g$  and less of the CTE about the  $T_g$ . The net results are an overall lower CTE from 0 to 290°C.



Figure 11. Effect of Tg on CTE

Silica has a much lower CTE than organic materials. The effect of varying levels and types of silica on CTE on epoxy and epoxy/PPE-M was evaluated. The effect of these variables on the overall CTE from 0 to 290°C is shown in Figure 12. The CTE for epoxy and epoxy/silica castings with 10, 25, and 40phr silica showed an average decrease in CTE of about 5, 10, and 15%, respectively. The SPH silica appears to be slightly more effective in decreasing the CTE. The addition of 30 and 50wt% PPE-M resulted in a decrease in overall CTE of 4 and 6%, respectively. Over the compositional range studied, the



combination of silica and PPE-M gave a reduction in the overall CTE up to 18%.

Figure 12. CTE versus silica and PPE-M

Water absorption in polymers is known to have adverse effects on dimensional stability,  $T_g$ , mechanical properties, and dielectric properties. The effect of silica loading and the amount of PPE-M on moisture uptake was studied by immersion of test specimens in water at 25°C. Only the ground silica (GRD) was used in this study. The moisture absorption results for epoxy/silica and epoxy/PPE-M appear in Figure 13. The moisture uptake decreases with increasing levels of silica and PPE-M. Over the composition range studied, the use of silica and PPE-M decreased the water uptake by 4-14 and 16-27%, respectively.



Figure 13. Effect of silica and PPE-M on water absorption

The combination of silica and PPE-M resulted in greater reductions in moisture absorption. Water uptake for epoxy/silica/PPE-M castings is shown in Figure 13. Over the composition range studied, the use of both of silica and PPE-M in the castings decreased the water uptake by 20-37%. These lower moisture absorption results suggest less change in dielectric properties on exposure to moisture.



Figure 14. Combined effect of silica and PPE-M on water absorption

The combination of silica and PPE-M were screened in laminates. Four laminates were prepared and characterized. Spherical silica (SPH) was used in formulations B and D. The formulations and properties are summarized in Table 14. The control, Formulation A, contained no silica or PPE-M. Formulations B contained silica. Formulation C contained PPE-M. Both silica and PPE-M were used in formulation D. Based on these laminates, both by themselves silica and PPE-M lower D<sub>k</sub>, D<sub>f</sub>, and Z-axis CTE. However, the largest decreases were noted with the combination of silica and PPE-M. Indeed, compared to formulation A, D exhibited an 11% decrease in D<sub>k</sub>, 50% decrease in D<sub>f</sub>, and a 20% decrease in CTE.

Resin Formulation	А	В	С	D
DGEBPA, wt%	50	50	25	25
Br Epoxy, wt%	50	50	25	25
PPE-M, wt%	0	0	50	50
Reinforcing Agents				
Glass cloth, phr	100	100	100	100
Silica, phr	0	50	0	50
Laminate Characterization	on			
Ash, wt%	52.3	61.5	51.2	62.2
Thickness, mm	1.22	1.24	1.21	1.22
$T_{g}, ^{\circ}\mathrm{C}$	138	140	167	168
D <sub>k</sub> @ 1 GHz	4.22	3.99	3.78	3.75
D <sub>f</sub> @ 1 GHz	0.0112	0.0099	0.0072	0.0059
Z-axis CTE, ppm/°C	82.76	67.77	78.17	65.82

#### Table 3. Formulation and properties of laminates

#### Conclusion

The performances of epoxy/silica, epoxy/PPE, and epoxy/PPE/silica were quantified using structure-property evaluations in castings. The effect of silica filler and PPE macromonomer in epoxy resin on some properties of was complimentary. Silica increased the density, flexural modulus and strength. PPE-M decreased the density, flexural modulus and strength. Silica lowered the notched impact strength. PPE-M increased the notched impact strength. D<sub>k</sub> was increased by silica and decreased by PPE-M. For some properties, silica filler and PPE macromonomer worked in conjunction to enhance properties. Both lowered the overall CTE, decreased the loss tangent, and lowered the moisture uptake. Clearly, these results suggest benefits in using silica and PPE-M together. Some differences were noted in performance of some of the silicas used in this study.

These performance attributes were demonstrated in epoxy-based laminates. The combination of silica and PPE-M resulted in significant decreases in dielectric properties and CTE.

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# Polyphenylene Ether Macromonomer. VIII Low Z-Axis CTE, Low Df Epoxy Laminates

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# **ELECTRONIC PACKAGING**

### **TRENDS – Performance & Environmental:**

Increased density – more functionality in less real estate. ECO friendly products



**INCREASED DEMANDS on DIELECTRIC MATERIALS** 



## **DIELECTRIC MATERIALS**



"Performance"

Enhance the performance of epoxy resin Application to epoxy hybrids & non-epoxy

Enhance performance with Silica and PPE macromonomer (PPE-M)



### WHY SILICA and PPE?

### **Key Components in Laminate**



### Silica:

- Used in EMC and encapsulant formulations
- Off-set cost of expensive non-halogen FRs
- Smoother surface

Use Silica and PPE macromonomer (PPE-M) for low Z-Axis CTE, Low D<sub>f</sub>/D<sub>k</sub> Epoxy



### **PPE-M**

**Polyphenylene Ether Macromonomer** 

Telechelic macromonomer - terminally functional, linear, large monomer



**PPE-M** 

### **PPE-M Features**

Bi-functional PPE Low molecular weight PPE High solubility in MEK and epoxy Reacts with epoxy resins Inherent flame resistance

### 2009 IPC/APEX Conference PPE-M in epoxy resins

- Increased toughness
- > Higher Tgs
- Lower dielectric properties
- Lower moisture uptake

### 2010 IPC/APEX Conference

- Decrease FR
- Improve properties

### **Broad enhancements in performance**



### QUARTZ – SILICA – SiO<sub>2</sub>



Four types of silica used in studyGround quartz = GRDSpherical = fused = SPHDiatomaceous Earth = DE



### MICROSCOPY OF SILICAS Scanning Electron Microscopy (SEM) x5000









### Ground quartz = **GRD** Platey (ground) = **PLA** Spherical = fused = **SPH** Diatomaceous Earth = **DE**

### **PARTICLE SIZE ANALYSIS**

APEX

IPC



Similar particle size



## **COMPARISON OF SILICAS**

DESIGNATION	SPH	PLA	GRD	DE			
Shape	Spherical	Platey	Ground	Diatoms			
Density, g/cc	2.2	2.65	2.65	2.3			
Particle Size							
D(4,3), μm	4.06	3.46	2.38	5.79			
D(3,2), μm	2.71	1.12	1.01	2.06			
D(v,0.1), μm	1.44	0.45	0.4	1.05			
D(v,0.5), μm	3.25	2.56	2.03	4.61			
D(v,0.9), μm	7.75	7.55	4.8	11.78			
Composition, % (from suppliers)							
SiO <sub>2</sub>	99.7	99.49	98.5	89.6			
Al <sub>2</sub> O <sub>3</sub>	-	0.102	1	4			
CaO	-	0.014	0.04	0.5			
MgO	-	0.021	0.02	-			
Na <sub>2</sub> O + K <sub>2</sub> O	<0.01	-	0.06	-			
TiO <sub>2</sub>	-	0.015	0.02	-			
Fe <sub>2</sub> O <sub>3</sub>	<0.01	0.039	0.09	-			

- D(4,3) equivalent volume mean diameter
- D(3,2) equivalent surface area mean diameter
- D(v,0.1) 10% of the volume distribution is below this value
- D(v,0.5) volume median diameter; 50% of the volume is below & below this value
- D(v,0.9) 90% of the volume distribution is below this value





### CASTINGS

### **Evaluation in castings**

- Resin only or resin/silica no glass fiber
- Unfettered by confounding factors from glass cloth

### GENERAL PROCEDURE

Disperse silica in MEK (14,000 rpm) Dissolve PPE-M (if any) in epoxy; warm to 60-70°C Add PPE-M/epoxy to Silica/MEK Add 2,4-EMI Remove MEK Place in press and cure

Catalyst: 1.5phr 2,4-EMI (2-ethyl-4-methyl imidazole)

Epoxy (BPA Epoxy): 100, 70, and 50wt% PPE-M: 0, 30, and 50wt% Silica: 0, 10, 25, and 40 phr



### FORMULATIONS

**PPE-M: 0, 30, and 50wt%** Silica: 0, 10, 25, and 40 phr Catalyst: 1.5phr 2,4-EMI

Wt% Resins + phr Silica Wt% Resins + wt% Silica

			_			
PPE-M,	Epoxy,	Silica,		PPE-M,	Epoxy,	Silica,
wt%	wt%	phr		wt%	wt%	wt%
0	100	0		0	100	0
30	70	0		30	70	0
50	50	0		50	50	0
0	100	10		0	90.91	9.09
30	70	10		27.27	63.64	9.09
50	50	10		45.45	45.45	9.09
0	100	25		0	80	20
30	70	25		24	56	20
50	50	25		40	40	20
0	100	40	1	0	71.43	28.57
30	70	40		21.43	50	28.57
50	50	40		35.71	35.71	28.57

Four types of silica used in evaluations Ground quartz = **GRD** Platey (ground) = **PLA** Spherical = fused = **SPH** Diatomaceous Earth = **DE** 



### DENSITY



• Silica increased densities (~2-4%)

• Densities decrease with increasing PPE-M 30% PPE-M 3-5% decrease

50% PPE-M 5-6% decrease

Silica increases density PPE-M lowers density



## **FLEXURAL MODULUS**



- Silica increased FM (~23-83%)
- PPE-M decreased FM (12-21%)
- Silica/PPE-M
  - 30% PPE-M decrease in FM (2-35%)

50% PPE-M + 24 & 40 phr silica increase in FM (2-13%)

Silica increases FM PPE-M decreases FM



### **FLEXURAL STRENGTH**



- Silica increased FS (9-40%)
- PPE-M decreased FS (8-15%)
- Silica/PPE-M

30% PPE-M/25-40 phr silica increase in FS (8-21%) 50% PPE-M/ 40 phr silica increase in FS (6%)

Silica increases FS PPE-M decreases FS



### **IMPACT STRENGTH**

Pendulum impact strength (Izod impact) - high-speed crack propagation Impact strength (IS) is higher for unnotched versus notched



Crack – stress concentrators Particulate fillers – stress concentrators



### **TOUGHNESS - Notched** Notched Izod impact strength



- Silica decreases notched impact strength (39-76%)
- PPE-M increases toughness (39-81%)
- Silica/PPE-M

Minimize the lost in toughness

Silica decreases notched Izod toughness PPE-M increases notched Izod toughness



### **TOUGHNESS - Unnotched**

**Unnotched Izod impact strength** 



Silica, phr

- Silica increases unnotched impact strength (34-120%)
- PPE-M increases unnotched impact strength (126-311%)
- Silica/PPE-M significant increases in toughness (127-540%)

Silica increases toughness PPE-M increases toughness



## **UNNOTCHED IMPACT versus FM**



Flexural Modulus, MPa

- Correlation between FM and unnotched impact strength
- Correlation coefficients 0.993-0.987

Increase in unnotched toughness related to modulus of matrix



### **UNNOTCHED IMPACT versus FS**



- Correlation between FS and unnotched impact strength
- Correlation coefficients 0.983-0.978

Increase in unnotched toughness related to strength of matrix



### **DIELECTRIC CONSTANT**

Relative Permittivity, D<sub>k</sub>



- Silica give a slight increases in D<sub>k</sub> (1.6-4.8%)
- **PPE-M lowers D<sub>k</sub>** (3-5%)
- Silica/PPE-M minimizes increase in D<sub>k</sub>
- Spherical silica better

Silica increases dielectric constant PPE-M lowers dielectric constant



## LOSS TANGENT



- **PPE-M lowers D**<sub>f</sub> (24-38%)
- Silica/PPE-M lowers D<sub>f</sub> (24-46%)
- Spherical silica better

Silica and PPE-M lower loss tangent



## **Effect of PPE-M on CTE**

P	PE-M Wt%	<i>T<sub>g</sub></i> ℃	CTE 0°C- <i>T<sub>g</sub></i> ppm/°C	CTE <i>T<sub>g</sub></i> -290° ppm/°C	C CTE 0-290°C ppm/°C
_	0 30 50	133 155 167	55.76 57.12 58.10	185.29 195.40 201.60	121.08 116.57 113.96
CTE, ppm	40000 35000 25000 20000 15000 10000 5000	-	0% F	PPE-M - ∑ 50%	PPE-M
	U L	0	50 100 Temj	150 200 Derature, °C	250 300
CTE below <i>T<sub>g</sub></i> << CTE above <i>T<sub>g</sub></i> PPE-M give a small increase in CTE PPE-M increases <i>T<sub>g</sub></i>					
СТІ	E <sub>0-29</sub>	O°C	= CTE <sub>0</sub>	<sub>C -<i>Tg</i></sub> + C	TE <sub>7g -290°C</sub>

50% PPE-M lower CTE 0-290°C > More CTE below  $T_q$ , less CTE above  $T_q$ 



### **Effect of SILICA and PPE-M on CTE**



- Silica lowers CTE (5-16%)
- PPE-M lowers CTE (4-6%)
- Silica/PPE-M lowers CTE (4-20%)
- Spherical silica better

**Combination of silica and PPE-M give lower CTE** 

# **EFFECT** of WATER



Moisture plays an important role in performance

- Alters thermo-mechanical properties
- Hygroscopic stress through differential swelling
- Reduces interfacial adhesion strength
- Induces corrosion
- Cause internal shorts through metal migration
- Increases dielectric properties

Water can hydrogen bond to hydrophilic moieties Cured epoxy resins contain alcohol groups

H<sub>2</sub>O absorption can cause integrity and reliability issues





### WATER UPTAKE versus TIME

### Immersion in water at 25°C

Silica = GRD



- Water uptake increases with immersion time
- Silica/PPE-M lowers H<sub>2</sub>O uptake

**Combination of silica and PPE-M give lower H<sub>2</sub>O uptake** 



### LAMINATES

Laminate Formulation	Α	В	С	D
Resin				
DGEBPA, wt%	50	50	25	25
Br Epoxy, wt%	50	50	25	25
PPE-M, wt%	0	0	50	50
2,4-EMI, phr	2.0	2.0	1.5	1.5
<b>Reinforcing Agents</b>				
Glass Cloth, phr	100	100	100	100
Silica, phr	0	50	0	50
Characterization				
Ash, wt%	52.3	61.5	51.2	62.2
Thickness, mm	1.22	1.24	1.21	1.22
<i>Τ</i> <sub>g</sub> , °C	138	140	167	168
Dk @ 1 GHz	4.22	3.99	3.78	3.75
Df @ 1 GHz	0.01199	0.00993	0.00715	0.00592
Z-axis CTE, ppm/°C	82.76	67.77	78.17	65.82

Note: "A" is similar to FR-4

**Prepared low Z-Axis CTE, Low Df Epoxy Laminates** 



### **SUMMARY**

### Blue = Beneficial effects = ↑ ↓ Red = Adverse effects = ↑ ↓

PROPERTY	Silica	PPE-M
Density	1	↓
Flexural Modulus	<b>^</b>	↓
Flexural Strength	<b>^</b>	↓
Notched Impact Strength	¥	<u>^</u>
Unnotched Impact Strength	1	1
Dielectric Constant	1	↓ :
Loss Tangent	.↓	V
$T_g$	0	<b>^</b>
CTE	↓	↓
H <sub>2</sub> O Absorption	↓	↓

### Silica and PPE-M can compliment each other



## **CONCLUSIONS**

# Silica can have positive effects on some properties

- ✓ Lower CTE
- ✓ Lower D<sub>f</sub>

## Silica can have an adverse effect on some properties

- o Decreased notched impact strength
- o Increased D<sub>k</sub>

## **PPE-M** can have positive effects on properties

- Lowered density (lower cost implications)
- ✓ Increase notched toughness (2ndary operations, more filler)
- $\checkmark$  Lower  $D_k$  and  $D_f$  (better performance)
- $\checkmark$  Similar or increased  $T_g$ s (better performance)

## Silica and PPE-M lower moisture absorption

- $\checkmark$  Less change in  $D_k$  and  $D_f$  (more stable performance)
- Reduced drying time for 2ndary operations (cost implications)

**Best performance with a combination of Silica and PPE-M**