Development of Halogen Free, Low Loss Copper-Clad Laminates Containing a Novel Phosphonate Oligomer

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Abstract

With the rapid development of the information industry, increasing attention is being paid to the dielectric performance of base materials including copper-clad laminates (CCL) and prepregs. In addition to the increasingly high performance requirements of CCL's, the present global attention to less toxic products is leading to an increase in the use of halogen-free flame retardants in electronics. The main flame retardants used in halogen-free CCL's are phosphorus-containing phenolic resins, phosphonitriles, phosphorus containing epoxy resins, and several additive type compounds. Flame retardant additives like phosphates have low or no reactivity with epoxy resins, which typically results in lower glass transition temperature (Tg), higher moisture absorption, reduced dielectric performance and lower heat resistance. This paper introduces a new phosphonate oligomer which can be used as a reactive flame retardant in epoxy based resin systems. Suitable conditions for the complete reaction between the phosphonate oligomer and epoxy resin are described and the resulting halogen-free laminates with improved properties such as low Df, low coefficient of thermal expansion (CTE), high peel strength, and good toughness are presented. The significance of this paper is not only to introduce a new halogen-free, mid-Tg, low loss CCL, but also to highlight a novel kind of halogen free reactive flame retardant for CCL. Comparison performance data to other commercial halogen-free base materials will be presented.

1. Introduction

The demand for high performance halogen-free CCL has been growing ever since the new millennium. The unabated technical trends to high performance are higher thermal resistance, higher Tg, and low CTE, lower water absorption for higher conductive anodic filament (CAF) resistance and reliability. In recent years, with the rapid development of telecommunication technology to well beyond 10Gbps and the ubiquitous application of mobile interconnections all over the world, the most demanding requirement is signal integrity, which is determined by the dielectric properties, dielectric constant (Dk) and dissipation factor (Df). As the CCL industry has transitioned from brominated to phosphorus based systems to achieve halogen-free flame retardant systems, the limitations of current phosphorus based systems are becoming increasingly evident. The commonly used phosphorus containing epoxy resins in the CCL industry are mostly derived from 9,10-dihydro-9-oxa-phosphaphenanthrene 10-oxide (DOPO), which is associated with susceptibility to delamination under lead free soldering processing due to its higher polarity and higher moisture absorption compared to brominated systems. DOPO based systems are also facing limitations in meeting the demanding requirement of lower Dk/Df performance. Therefore, the CCL industry is continually searching for new halogen-free flame retardants that enabled improved CCL performance at competitive prices.

This paper introduces a new phosphonate oligomer that can be used as a reactive flame retardant for epoxy resins used in CCL applications. DSC and FTIR evidence indicates that the curing reaction occurs between the secondary hydroxyl group of the epoxy resin and the phosphonate bond of the oligomer resulting in a crosslinked epoxy network. The mechanism and kinetics of curing of epoxy resins with poly(aromatic alkyl phosphonates) was reported in the literature. The proposed mechanism similarly suggested the curing occurs due to opening and insertion of the epoxy into the phosphonate bond. Halogen-free laminates containing the phosphonate oligomer showed improved thermal, mechanical and dielectric properties (low Dk/Df) could be achieved compared to the current commercial halogen-free CCL.

2. Experimental

2.1 Materials

Curing studies of the phosphonate oligomers (PO) were performed in Bisphenol A type epoxy resin (Product A) and phenolic type epoxy resin (Product B). The curing catalyst was 2-ethyl-4-methyl imidazole (24EMI). The properties of the phosphonate oligomers (PO1 and PO2) used in this study are shown in Table 1.

Properties	PO1	PO2
Appearance	white, coarse granules	white, coarse pellets
P content (wt%)	8.5	10.0
Hydroxyl group equivalent (g/eq)	650	1120
Mn (g/mol)	1300	2500
Free phenol (wt%)	<0.25	<0.25
Td (°C, 5% loss)	330	375
Solubility	Soluble in acetone,	Soluble in acetone,
	MEK, DMF	MEK, DMF

Table 1 – Properties of	phosphonate oligomers
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2.2 Test Methods

For the curing studies, DSC analysis were performed with production DSC analysis equipment. Curing was done in sealed aluminum pans and run at a heating rate of 10°C/min. FTIR spectra were obtained on production FTIR equipment, in Attenuated Total Reflectance (ATR) mode. A mixture of the epoxy resin and phosphonate oligomer was prepared in 40% MEK solvent. The catalyst (0.2 phr 24EMI) was added and the resin mixture poured into 6 aluminum pans (1 inch diameter). The pans were placed in an oven to remove the solvent at 100°C for 1 hour and then cured at 190°C for 3 hours. A single pan was removed every half hour to determine the extent of the reaction via FTIR.

The CCL properties were tested according to IPC and UL Standards as follows: (1) Glass transition temperature (Tg): Dynamic Mechanical Analysis (DMA) and Differential Scanning Calorimetry (DSC) at a heating rate of 10°C/min (2) Thermal decomposition temperature (Td): Thermogravimetric Analysis (TGA) (3) X, Y, Z-CTE and T288: Thermomechanical Analysis (TMA) (4) Dielectric constant (Dk) and dielectric dissipation factor (Df): SPDR (at 1.1, 3, 5, 10 GHz) and parallel plate capacitor (at 1 GHz) (5) Peel strength: IPC-TM-650 (6) Flammability test: UL 94

2.3 CCL preparation for testing

Varnish formulations containing a mixture of the epoxy resin and the phosphonate oligomer were prepared in MEK solvent. Combinations of the oligomer as the sole hardener and mixtures with various co-hardeners like phenolic curing agents were tested. Inorganic fillers like Alumina trihydrate (ATH) are added to the resin mixture, before adding the catalyst at the end. The varnish gel time (VGT) is measured at 171°C and used to adjust the catalyst level to ensure the gel time is about 250 seconds. The glass cloth is then impregnated by dipping into the varnish bath and then passed through a pair of metering rolls which removes excess varnish from the glass cloth. The saturated glass cloth is then placed in an oven to remove the solvent and pre-cured (B-staged) to make the prepreg. The B-staging temperatures from 160-190°C were tested to determine the optimal conditions. The prepreg properties including resin content, gel time and viscosity were evaluated. The CCL is prepared by placing multiple layers (typically 8) of prepregs in between two sheets of copper foil and placed in a hot press at 190-200 °C for 70-90 minutes.

3. Results

3.1. Curing Studies

The curing profile of epoxy resins with the phosphonate oligomers PO1 and PO2 was performed by DSC analysis. Figure 1 shows samples based on a 1/1 Epoxy(Product A)/PO2 mixture with varying amounts of 24EMI catalyst from 0 to 1 phr. As expected, the curing exotherm occurs at the highest temperature (peak at 238°C) and the broadest temperature range for the mixture without catalyst and decreases with increasing catalyst content. The reaction with 1 phr catalyst occurs significantly faster, with a peak exothermic temperature that is 60°C lower than the mixture without catalyst. Figure 2 shows DSC curves for two samples of (Product B)/PO1 and (Product B)/PO2 at a 3% P content with 0.2 phr 24EMI catalyst. The curves shows no difference in the curing exotherm temperatures between PO1 and PO2, indicating the hydroxyl content is not a significant factor in the curing reaction.



FTIR analysis was used to examine the reaction between the epoxy resin and PO by monitoring two main peaks as shows in Figure 3. The curing temperature was set at 190°C. The first peak is the disappearance of the C-O stretching peak at 933 cm-1 due the epoxy ring opening. The second peak is the appearance of a new C-O stretching peak in P-O-CHR at 985 cm-1 formed due to the reaction of the secondary hydroxyl group of the epoxy after ring opening at the P-O-Ar (aromatic) bond of the phosphonate oligomer.



Figure 3 - FTIR spectra of epoxy-phosphonate oligomer samples during curing at 190°C

3.2 Equivalent weight analysis

A reactive equivalent weight of 141g/equiv. for PO2 was calculated based on both phenolic hydroxyl content and the phosphonate (-OPO-) content of the phosphonate oligomer. The effect of varying stoichiometric ratios of PO2 to epoxy (Product 3) on Tg of the cured sample was studied. The phosphonate oligomer PO2 was first dissolved in MEK and mixed

into the epoxy resin before adding 0.5wt% catalyst, 2-methyl imidazole (2MI). The varnish was used to coat one sheet of glass fabric (7628), which was then baked in an oven at 200 °C for 90 minutes. The resulting Tg's for stoichiometric ratios ranging from 0.5 to 3.0 are shown in Figure 4.



Stoichiometric ratio of PO2 to epoxy

Figure 4 - Tg versus equivalent ratio of PO2 to epoxy resin

The DSC results indicate the maximum Tg of 170°C was obtained at a stoichiometric ratio of 0.8-0.9. At ratios below 0.8, a decrease in the Tg is a result of the incomplete reaction due to excess unreacted epoxy groups, which also lowers the crosslink density. At ratios greater than 1.0, the Tg decreases due to the plasticization effect resulting from excess unreacted phosphonate groups.

3.3 Effect of catalyst concentration

The effect of catalyst (2MI) concentration on the Tg at a stoichiometric ratio of 1.0 (phosphonate oligomer (PO2) to phenolic epoxy) is shown in Figure 5. Samples were cured at 200 °C for 90 minutes. The Tg exhibits an upward parabolic trend with a peak at 170 °C when the catalyst level is 0.6 wt%.



Figure 5 – Effect of 2MI catalyst content on Tg

3.4 Formulation Study

In addition to flame retardant and thermal properties, the dielectric properties of copper-clad laminates are becoming increasingly important for high speed and high frequency applications. Currently values of Dk 3.9-4.0 and Df 0.007- 0.009

represent a large share of the current market share. Generally, there are three ways to reduce Dk and Df of CCL. The first way is by reducing the Dk of the glass fiber reinforcement, for example, by making use of special low Dk glass fiber. Unfortunately, low Dk glass is expensive, costing multiple times more than conventional E-glass. The second is to reduce the Dk and Df of organic components of the formulation. This includes the base resin and the hardener system, as well as the flame retardant. Table 2 lists the Dk and Df values of the most common polymeric materials used for CCL and shows epoxy and phenolic resins have the highest Dk/Df values. The third way is to adopt a low Dk and Df filler like fused silica, hollow spherical micro-glass balls and some polymeric micro powders.

Resin	Dk	Df	Resin	Dk	Df
Ероху	3.0~3.9	0.010~0.030	Liquid Crystal Polymer (LCP)	2.9	0.002
Phenolic resin	3.1~4.0	0.030~0.037	Hydrocarbon Resin	2.2~2.6	0.001~0.005
Benzoxazine	3.0	0.008	Modified Polyphenylene Oxide (PPO)	2.45	0.0007~0.001
Cyanate resin	2.7~3.2	0.004~0.010	Cyclic Olefin Copolymer (COC)	2.3	0.00007
Polyimide (PI)	2.7~3.2	0.005~0.008	Poly(p-phenylene sulfide (PPS)	3.0	0.002
Bismaleimide (BMI)	2.8~3.2	0.005~0.007	Poly(ether sulfone) (PES)	3.5	0.003
Silicone resin	2.8~2.9	0.002~0.006	Poly(ether ether ketone) (PEEK)	3.2	0.003
Polyester resin	2.7~3.2	0.005~0.020	Polytetrafluoroethylene (PTFE)	2.1	0.0004

Table 2 -	Dk/Df of	various	resins
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3.5 CCL Properties

CCL samples containing phosphonate oligomer as the flame retardant and hardener system were tested according to standard IPC test methods. The properties of the phosphonate oligomer based system are shown in Column A of Table 3. The laminates were prepared using 8 ply of 7628 glass fabric. Column C shows comparative properties of a commercial halogen-free, mid-Tg, low Dk, CCL product. In addition to the strong flame retardant properties of the phosphonate oligomer based system, the CCL has excellent thermal resistance indicated by very low Z axis-CTE (Figure 6), improved soldering thermal shock and much higher (>400°C) thermal decomposition temperature (Figure 7).

Property		A (PO based)	C (Control)	
Tg (°C)	DSC	Tg1: 163.1/ Tg 2: 164.9 △Tg: 1.8	155	
	ТМА	151	145	
	DMA	164	168	
CTE-Z (ppm/°C)	α1/α 2	21/133	40/230	
СТЕ (%), 50-260°С	TMA	1.7	2.9	
T-288 (minutes)	with copper	>60	>60	
Td-5% (°C)	TGA	407	385	
Peel Strength (N/mm)	lounce, A	1.38	1.35	
Interlayer adhesion	Vertical	0.41-0.60	0.25-0.48	
Pressure Cooker Test (PCT)	E-1/105 105KPa/180min	>300	>300	
Soldering, minutes	288°C, with Cu	>5	>5	
Flammability	UL 94	t_1 :0.5;1.2;1.2;0.4;0.6 t_2 :5.1;4.5;5.4;6.8;5.4	t_1/:3.4;2.2;4.0;5.2;4.4 t_2/:5.7;6.7;6.6;5.8;5.8	
5		V-0	V-0	

able 3 - Comparative properties of PO-based laminate with commercial halogen-free



Figure 6 - TMA showing Z-CTE



Figure 7 - TGA showing thermal decomposition temperature (Td)

The modulus of a specimen, as measured by DMA, is a good indication of the rigidity of the CCL. As the mechanical modulus depends on the glass fabric type and the resin content of the specimen tested, a varnish cast sample without glass fiber was used for comparison. Varnish castings of the new formulation containing PO2 were prepared and used to measure the modulus using DMA. Figure 8 shows the storage modulus of the varnish castings compared to a conventional commercial halogen-free, mid-Tg CCL. The thickness of the cast samples is 1.7mm. The data shows significant increase in the modulus of the PO2 system compared to the control in the temperature range studied.



Figure 8 - DMA of varnish casting specimens without reinforcement

3.6 Dk and Df

Dk/Df values depend on the glass fabric type, resin content and specimen thickness. For example, it is known that the Dk of the glass fabric is much higher than that of the resin matrix for most of the CCL grades. Therefore, in order to avoid the resin content discrepancy due to the use of different glass fabric types, specimens were cast from the varnish without glass fiber and used to directly compare Dk and Df values. Castings of 1.70mm thickness were prepared from 3 formulations A, B and C. Formulation A is the PO based formulation, while B is a conventional commercial halogen-free, mid-Tg CCL and Formulation C, used to obtain the control CCL properties shown in Table 3, is a low Dk, halogen-free, mid-Tg CCL. The Dk and Df test results of varnish castings made from A, B and C are shown Figure 9 and Figure 10 respectively. The Dk value of A is comparable to that of the low Dk system C, and the Df of the PO based system A is much lower than that of B and C.



Figure 9 - Dk of A, B and C





Frequency and temperature dependence of Dk and Df for the PO-based CCL was tested with a CCL specimen of 5*2116 construction. The results shown in Figure 11 and Figure 12 indicated both Dk and Df of the laminate are relatively stable in the 2-10 GHz frequency range.



Figure 11 - Frequency dependence of Dk



Figure 12 - Frequency dependence of Df

4. Conclusions

Formulations containing a novel phosphonate flame retardant oligomer were used in the preparation of halogen-free copper clad laminates. The phosphonate oligomer functions not only as an effective flame retardant for the epoxy resin, but also as a reactive hardener. Properties of the resulting CCL show low Dk and significantly lower Df properties can be achieved when compared to current commercial halogen free CCL. The laminates also show improved thermal resistance and mechanical properties.

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- Targets
- Phosphonate Oligomers
- Curing Studies in Epoxy
- Evaluation of CCL Properties
- Summary





Current Commercial Halogen Free CCL Dielectric properties:

- Dk: 3.9-4.0
- Df: 0.007-0.009
- □ New demands for high performance, halogen free PCBs require:
 - improved signal integrity: lower Dk/Df
- □ In addition:
 - higher thermal resistance
 - higher Tg
 - lower CTE
 - lower moisture absorption







Phosphonate Oligomers

Features

- Flame Retardant Additive or Reactant
- Solid, white granules/pellets
- Range of molecular weight (Mn 1500-5500 g/mol, PS Standards)
- Phosphorus content 8.5 10.0 wt%
- Contains phenolic-OH endgroups
- Good solubility in wide range of organic solvents







Typical Properties

Typical Properties	Unit	PhosphonatePhosphonaOligomer 1Oligomer 2(PO1)(PO2)	
Appearance	-	coarse granules, white	coarse granules, white
Phosphorus Content	wt %	8.5	10.0
Average Molecular Weight (Mn)	g/mol	1500	2500
Glass Transition Temp	°C	85	85
Hydroxyl group equivalent	g/equiv	650	1120
Td, 5wt% weight loss	°C	330 375	
Optical Characteristics	-	Transparent Transparen	
Soluble in:	-	MEK, Acetone Methyl cellosolve (2-Ethoxyethanol) DMF	
Insoluble in:	-	Water, hexane	





Melt Viscosity of Oligomers



Phenol Novolac (PN) hardener Bis A Novolac resin (BN) hardener





Benefits in CCL Processing

- High solubility in typical organic solvents used for processing
- Highly compatible with epoxy resin systems
- Multi-functional reactivity with epoxy
- Low melt viscosity
- Improves compatibility with filler additives like silica
- Yields excellent prepreg surface quality
- Acts as both flame retardant and hardener







Curing Studies in Epoxy

DSC Curves of Bis-A Epoxy Resin (Product A)/PO2 (1:1) with 2E4MI at 0-1phr levels







Curing Studies in Epoxy

DSC Curves of Phenolic type epoxy resin (Product B)/PO1/PO2; 0.2wt% 2E4MI, OL (3%P)







FTIR Analysis of Curing Reaction

Method:

- Production Instrument: FTIR
- Mode: Attenuated Total Reflectance (ATR)







Monitoring Curing via FTIR

Two main peaks are monitored during the curing process:

- Loss of epoxy ring C-O stretching peak due to epoxy ring opening reaction
- Formation of RHC-O-P due to reaction of secondary OH at O-P=O site







Curing Kinetics

OCN-EP Phenolic type epoxy resin (Product B), 190°C, 0.2wt% 2E4MI, PO1/PO2 (3%P)



- ✓ PO1 and PO2 have similar reactivity
- Curing reaction occurs via phosphonate groups in the oligomer backbone





Reactive Equivalents

Reactive Equivalent is based on reaction at both phenolic-OH endgroups and phosphonate groups on the oligomer backbone

Product	OH # (mg KOH/g)	OH Equiv weight (g/eq)*	OL Reactive Equiv weight (g/eq)**
PO1	85	660	138
PO2	50	1120	141

- * Based only on phenolic-OH
- ** Based on both phenolic OH + phosphonate groups





Tg Analysis of Cured Samples

Cured at 200°C for 90 min



Epoxy (Product 3), 0.5wt% 2-Methyl Imidazole (2MI)



Prepreg and CCL

Features

- Good visual cosmetics/appearance of prepreg
- Good dielectric properties
- Low Z-CTE
- High peel strength
- Good heat resistance



prepreg



copper-clad laminate





Evaluation of CCL Properties

Property		A (PO2 based)	C (Control)
	DSC	Tg1: 163.1/Tg 2: 164.9 △Tg: 1.8	155
rg (°C)	ТМА	151	145
	DMA	164	168
CTE-Z (ppm/ºC)	α1/α 2	21/133	40/230
CTE (%), 50-260 °C	ТМА	1.7	2.9
T-288 (minutes)	with copper	>60	>60
Td-5% (ºC)	TGA	407	385
Peel Strength (N/mm)	1ounce, A	1.38	1.35
Interlayer adhesion	Vertical	0.41-0.60	0.25-0.48
Pressure Cooker Test (PCT)	E-1/105 105KPa/180min	>300	>300
Soldering, minutes	288⁰C, with Cu	>5	>5
Flammability	UL 94 (1.6mm)	t_1 :0.5;1.2;1.2;0.4;0.6 t_2 :5.1;4.5;5.4;6.8;5.4 Sub-T1: 3.9; Sub-T2:27.2 Total T: 31.1	t_1 :3.4;2.2;4.0;5.2;4.4 t_2 :5.7;6.7;6.6;5.8;5.8 Sub-T1: 19.2 Sub-T2: 30.6 Total T: 49.8
		V-0	V-0





Z axis-CTE (DMA)





8 ply-7628



Modulus by DMA

Test samples: Varnish castings without reinforcement – 1.7mm thickness







Dielectric Properties

Test samples: varnish castings of:

- A PO2 based formulation
- **B** mid-Tg, halogen free, commercial control
- C mid-Tg, halogen free, low Dk, commercial control







Dk and Df versus Frequency

PO2-based Formulation



5 ply - 2116





Moisture & Heat Resistance

РСТ		NSCC	-F1			
(E-121ºC/105KPa)	Solder dip @ 288°C		Water Absorption			
180 min	> 300 s		> 300 s		().69%
85°C & 85% RH treatment, thermal shock		C-120/85/85 288°C/10s testing	cycles	>10; >10; >10		
85°C & 85% RH treatment, moisture picking-up	144hrs	E-1/105+ C-120/85/85	-	0.57%		
85°C & 85% RH treatment, thermal shock	168hrs	C-144/85/85 288°C/10s testing	cycles	>10; >10; >10		
85°C & 85% RH treatment, moisture picking-up		E-1/105+ C-144/85/85	-	0.56%		
85°C & 85% RH treatment, thermal shock	102bm	C-168/85/85 288°C/10s testing	cycles	>10; >10; >10		
85°C & 85% RH treatment, moisture picking-up	1921112	E-1/105+ C-168/85/85	-	0.57%		





- Phosphonate oligomers are an effective FR and hardener for epoxy-based resins used in CCL applications
- In addition to achieving flame retardancy (V0), resulting CCL have improved properties over current commercial non-halogen epoxy based systems:
 - Very good dielectric properties low Dk (3.5) and Df (<0.007)
 - Low CTE
 - Very high thermal stability (Td >400°C)
 - High peel strength
 - Increased toughness (modulus)
 - Good moisture and heat resistance

