

# New Phosphorus-based Curing Agents for PWB

A. Piotrowski\*, M. Zhang\*, Y. Zilberman\*\*, Eran Gluz\*\*, S. Levchik\*

\*ICL-IP, Tarrytown, NY, USA

\*\*IMI (Tami) Institute for R&D Ltd., Haifa, Israel

## Abstract

As a result of the continuous industrial trend towards high density packaging there is a growing demand for highly thermally-stable laminate materials. Although the epoxy resin defines the thermal stability, often the flame retardant used becomes the limiting factor in achieving a higher stability. Recognizing this industrial need, the company has developed a new flame-retardant curing agent, Material A. This is a phosphorus-based polymer which cures epoxy via a very specific mechanism. Common Novolac epoxy resins cured with Material A and a phenol-formaldehyde resin show a  $T_g > 180$  °C and  $T_d > 400$  °C. In addition to a high thermal stability, Material A also shows a dielectric loss factor lower than commercial phosphorus-based flame retardants.

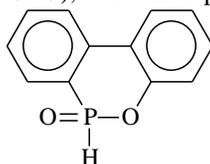
## Introduction

Epoxy resins are widely used in both industrial and consumer electronics because of, among other things, their chemical resistance, mechanical strength and electrical properties. To be useful for these applications, the epoxy resins must provide ease of handling and possess a certain physical, thermal, electrical insulation and moisture-resistant properties. For example, epoxy resins showing high thermal stability and high glass-transition temperature, while maintaining low dielectric constant and low dielectric loss possess a desirable combination of properties for electronic applications, especially in high temperature environment, like engine controls etc.

Epoxy resins, however, are flammable. As such, different approaches have been made to imparting the desired level of flame resistance to epoxy resins. Such approaches entail the employment of either halogen-containing flame-retardant compounds or recently halogen-free flame-retardant compounds. Halogenated compounds have a proven track and work well in most applications, however, they are now undergoing additional scrutiny, and industry is using various non-halogenated compounds, mostly phosphorus-based as an alternative to brominated FR. Although halogen-free systems have still challenges with ever rising requirements for moisture sensitivity, in some applications halogen-free solutions can provide better properties for some applications.

Most flame retardants have a negative effect on many physical and electrical properties of PWB. Thus the main challenge for flame retardants is finding materials that satisfy all of the electrical, thermal, chemical, and mechanical properties required for optimal device performance. Since P based flame retardants are more efficient than Br based flame retardants they can be used in significantly lower level thus minimizing the negative effect.

Although many chemicals were considered as potential halogen-free flame retardants, the majority formulations use 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), either incorporated in epoxy resin or in curing agent.



Structure of DOPO

**Table 1 - Commercial phosphorus-based PWB flame retardants**

Product name	Description	Advantages	Drawbacks
DOPO	Monofunctional reactive phosphinate	Relatively inexpensive, reliable track for simple FR4 formulations.	Must be pre-reacted with epoxy, higher cost, limited formulation changes
DOPO-HQ	Product of reaction of DOPO and benzoquinone	Good electrical properties, efficient	Low solubility, must be pre-reacted, Higher cost after reaction with epoxy
Cyclic phenoxyphosphazenes	Additive	Excellent electrical properties.	Low Tg, acts as a plasticizer, high cost
DOPO-BPA	Product of reaction of BPA formaldehyde and DOPO	Works well in mid-range Tg with good thermal stability. High %P. Flexibility in formulating	Requires fillers to improve Tg and pressure cooker performance
Di DOPO	Two DOPO units connected by ethylene bridge Unreactive	Good electrical properties, flexible in formulating.	Solid used as a filler, must be well dispersed.

In Table 1 there is only one example of a phosphorus-based flame retardant which is not DOPO based, i.e. the cyclic phenoxyphosphazenes, which have to be used at much higher phosphorus levels than DOPO-derived flame retardants.

DOPO is a reactive monofunctional molecule and it can be incorporated into the epoxy network. In order to make effective use of DOPO, it needs to be pre-reacted with multifunctional epoxies. Such pre-reacted epoxy has much fewer reactive sites resulting in lower Tg.

Such a pre-reacted DOPO epoxy is low in %P, which drastically limits any formulation changes. A recently-developed derivative of DOPO and bisphenol A has a much higher %P and is soluble in common solvents such as MEK. This product is di-functional, which improves the crosslink density, resulting in a higher Tg. DOPO-BPA is a significant step forward into better performance. However, achieving Tg >170 °C and thermal stability >370 °C is very difficult with this product and most formulations use fillers to achieve a solid V-0.

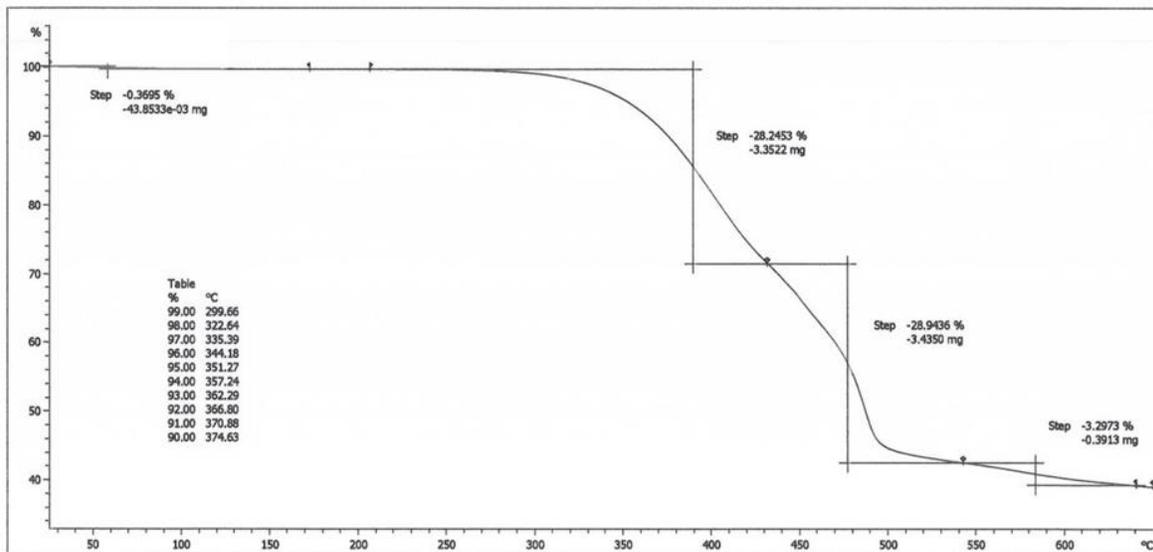
Recognizing need for high thermal stability PWB, the company has developed a new flame-retardant curing agent that provides the desired level of flame retardancy, high glass transition temperature (Tg) and high thermal stability of a thermosetting resin, such as an epoxy resin. Although use of flame retardants usually has a detrimental effect on the electrical properties, Material A provides a cured resin with a low Dk and a reasonably low Df. Since Material A is compatible with low Dk resins, this enables the preparation of laminates with excellent electrical properties.

**Table 2 - Physical properties of Material A**

Property	Value
Appearance	Light brown flakes or powder
Chemical nature	Polymer
Softening temperature, °C	>130
Phosphorus content	6.5-7%
T <sub>g</sub> , °C	130
Molecular weight, Mw	~1200
Thermal stability, TGA 5% wt. loss, °C	340-355
Solubility in MEK	>40%
Solubility in acetone	>40%
Viscosity of 60% MEK solution	710 cp
Viscosity of 70% acetone solution	1900 cp
Varnish viscosity at 60% solids	220 cp
Reactive equivalent	220
Functionality	Multifunctional
FR efficiency unfilled system, V-0	2-2.5 wt.% P
Application with epoxy	Curing agent

Material A is a very stable molecule even before cure and because it is a polymer it has a relatively high T<sub>g</sub> of ~130 °C on its own.

Figure 1 shows a typical TGA of Material A in nitrogen. It starts to decompose at about 300 °C and leaves about 40 % solid residue at 500 °C.



**Figure 1 - TGA of Material A, Heating rate 10 C/min, nitrogen flow**

### Laminate preparation

Material A was explored as a co-curing agent for epoxy-laminate applications. Material A, together with phenolic Novolac, was used to cure the multi-functional phenol Novolac epoxy resin (PEN) and cresol Novolac epoxy resin (CEN). All the information on the materials is listed in Table 3. The solids content of the varnish was maintained at 67% with the addition of a MEK/Dipropylene Glycol Methyl Ether (80/20) solvent mixture. A varnish formulation was prepared therefrom, which had a phosphorous content of 2.4% (dry solid) and the composition of which is shown in Table 4.

**Table 3 – Materials used in laminate preparation**

Name	General Information	Function
SD-Novolac	Phenolic Novolac (PN)	Curing agent
PEN	Phenol Novolac epoxy (PEN)	Epoxy resin
CEN	Cresol Novolac epoxy (CEN)	Epoxy resin
Methyl ethyl ketone	Butan-2-one	Solvent
Dipropylene Glycol Methyl Ether	1-Methoxy 2-propanol	Solvent
Dimethyl formamide	N,N-Dimethylformamide	Solvent
2-MI	2-Methyl imidazole	Catalyst
Glass Cloth	E-Glass	Reinforcing agent
Copper foil	Electrodeposited, 1.0 oz./ft <sup>2</sup>	Resistance to oxidation in warm and humid environments and for precise etching behavior, and other

**Table 4 - Epoxy-laminate Formulation 1**

PEN (wt %)	CEN (wt %)	Material A (wt %)	PN (wt %)	2-MI (wt %)
24.3	29.7	35.8	10.2	0.02

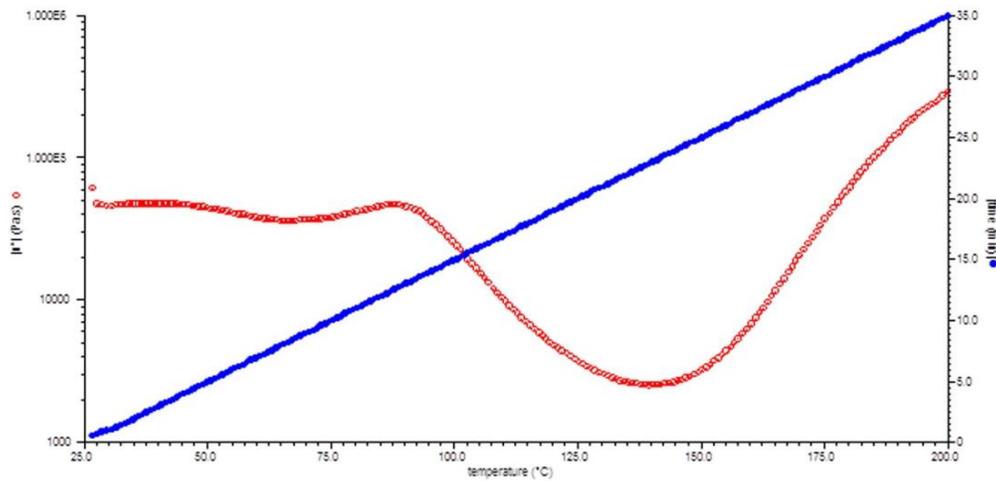
The addition of the catalyst was carefully controlled by adding small incremental amounts of 2-methylimidazole (2 MI) solution (20 weight% solids) in DMF to obtain an optimum varnish gel time of 270 seconds at 171 °C, according to IPC-TM-650 test 2.3.18.

Prepreg was prepared using a glass fabric (18 inches x 72 inches) continuously passed through a trough containing the varnish and through squeeze rolls, such that a uniform coating was obtained. Sections of the coated fabric were hung in the hood overnight for slow evaporation of the solvent. Prepregs were made by drying the resin-coated glass fabric in a preheated air-circulated oven at 160 °C for four minutes and thirty seconds, which gave a resin flow of less than 20.0%. Also, the resin content was controlled to be above 50-55%. The prepreg properties are shown in Table 5 below:

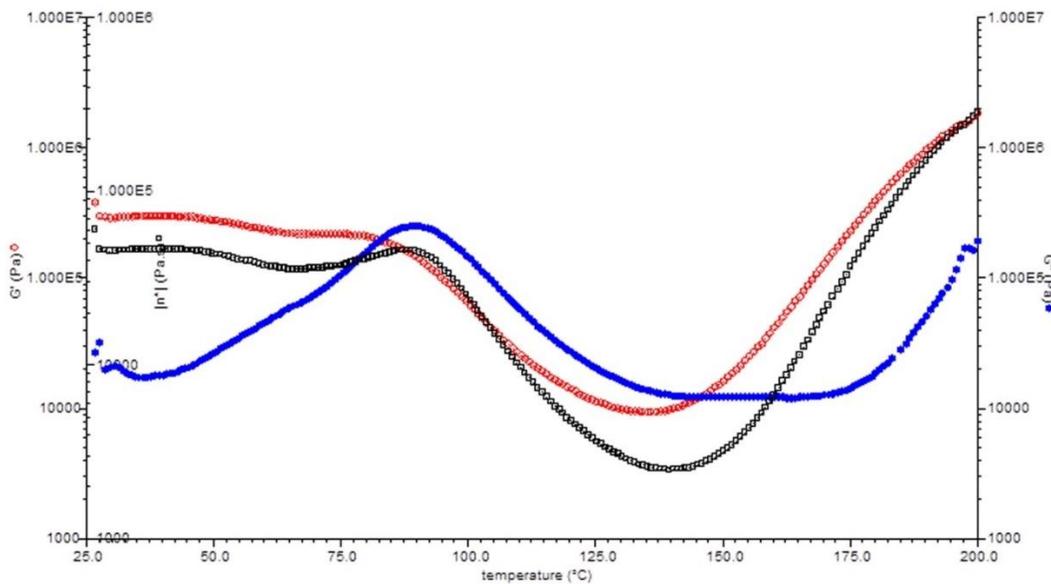
**Table 5 - Properties of prepreg with Material A for the Formulation 1**

Formulation of Material A as shown in Table 4	IPC-TM-650 No.	Value
Resin content (wt %)	2.3.16.2	50-55
Varnish gel time (sec)	2.3.18	270
Prepreg gel time (sec)	2.3.18	81
Resin Flow (%)	2.3.17	<20

Figure 2 shows the complex viscosity profile of the prepreg with the rise in temperature of the B-staged resin system in an oscillatory testing mode. Figure 3 shows the overlay curves for the storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $|\eta|$ ) of the B-staged resin system.



**Figure 2 - Complex viscosity profile of the prepreg**



**Figure 3 - Overlay curves for the storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $|\eta|$ ) of the B-staged resin system**

Based on Figures 2 and 3, the curing cycle was designed to obtain a good resin flow. A low initial pressure of 10 psi was applied at 103-105 °C (the complex viscosity of the prepreg was around 17560 pa-s) and sufficient to ensure the required resin flow as studied during the preparation of various experimental epoxy laminates. Subsequently 20 psi pressure was applied at 140 °C and the pressure was maintained at 20 psi until 165 °C. The pressure was again raised to 50 psi at 165 °C and 100 psi once the press reached 175 °C. A pressure of 100 psi was applied at 175 °C and finally a pressure of 220 psi was applied at 195 °C.

Finally, the press was maintained at 220 psi and 195 °C isothermally for 90 minutes. The laminate showed a good resin flow and the thickness of the final laminate was close to 1.3 mm (without copper). The laminate was rated as V-0, with a maximum burn time of 7 seconds, by following ASTM D3801-10 standard using a production UL-94 burning chamber (V-0 being the highest possible rating).

The laminate was also prepared using only PEN, and not a blend of PEN and CEN, using the following composition and similar conditions to those described above.

**Table 6 - Formulation with PEN (Formulation 2)**

PEN (wt %)	Material A (wt %)	PN (wt %)	2-MI (wt %)
50.9	36.8	12.5	0.02

The basic properties of both laminates are listed in Table 7.

**Table 7 Comparative properties of laminates prepared with Formulations 1 and 2 and commercial halogen-free system 3<sup>7</sup>**

Formulation	1	2	3 <sup>7</sup>
Flammability <sup>1</sup>	V-0	V-0	V-0
Water absorption RT 24 hr <sup>2</sup>	0.06	0.07	0.2
PCT 60 min water absorption % <sup>3</sup>	0.22	0.24	0.69
PCT 120 min water absorption % <sup>3</sup>	0.36	0.38	
288 °C PCT 60 min <sup>3</sup>	>20"	>10'	<10" failed
288 °C PCT 120 min <sup>3</sup>	<10" failed	>10'	
Peel strength (pounds/inch of width) <sup>4</sup>	8.3	7.7	9.0
Tg DMA	192	183	175
Tg TMA	170		150
CTE ( $\alpha_1$ , $\alpha_2$ ) <sup>5</sup>	33.7; 234.3	52.1; 307.2	
Td (5% wt. loss) °C	416	412	394
T288 min <sup>6</sup>	>60		>30

<sup>1)</sup> UL 94; <sup>2)</sup> IPC-TM-650, Method 2.6.2.1; <sup>3)</sup> Test procedure IPC-TM-650, Method 2.6.16

<sup>4)</sup> Test procedure IPC-TM-650; Method 2.4.8; <sup>5)</sup> Test Procedure: IPC-TM-650, Method 2.4.25

<sup>6)</sup> Test procedure IPC-TM-650, Method 2.4.24.1

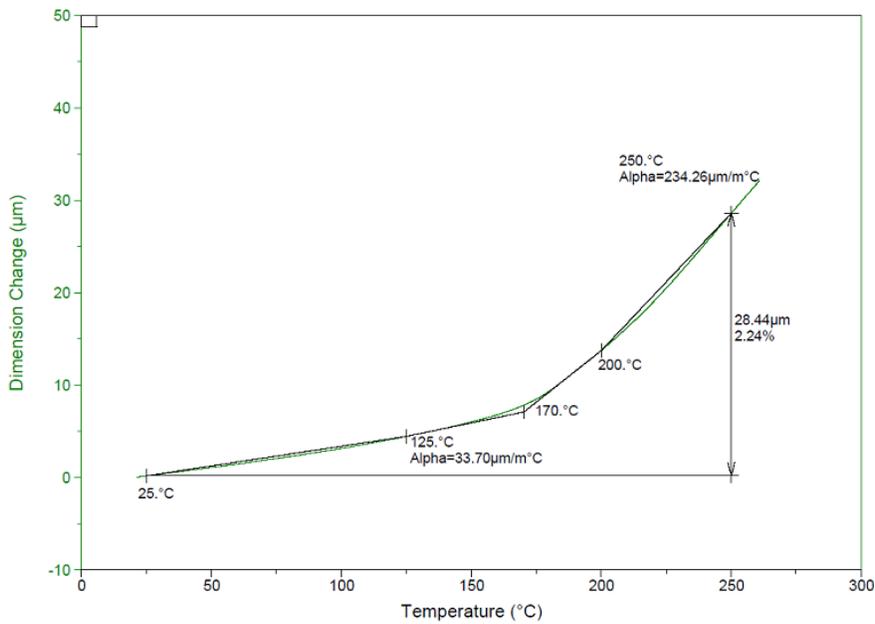
<sup>7)</sup> Formulation 3 is prepared using PEN, CEN, Material B (commercial halogen-free and phosphorus-based compound), and DICY

Both laminates have a very low room-temperature water-uptake of 0.06 and 0.07 respectively, and a low water-uptake after being in an autoclave for 120 min. Surprisingly, the sample with PEN alone performed better in the PCT test, and no delamination was observed on 5 samples after 120 minutes in the autoclave, and after submersion in molten solder at 288 °C for 10 minutes. Laminate prepared with epoxies mixture passed the test after 60 minutes but failed after 120 minutes.

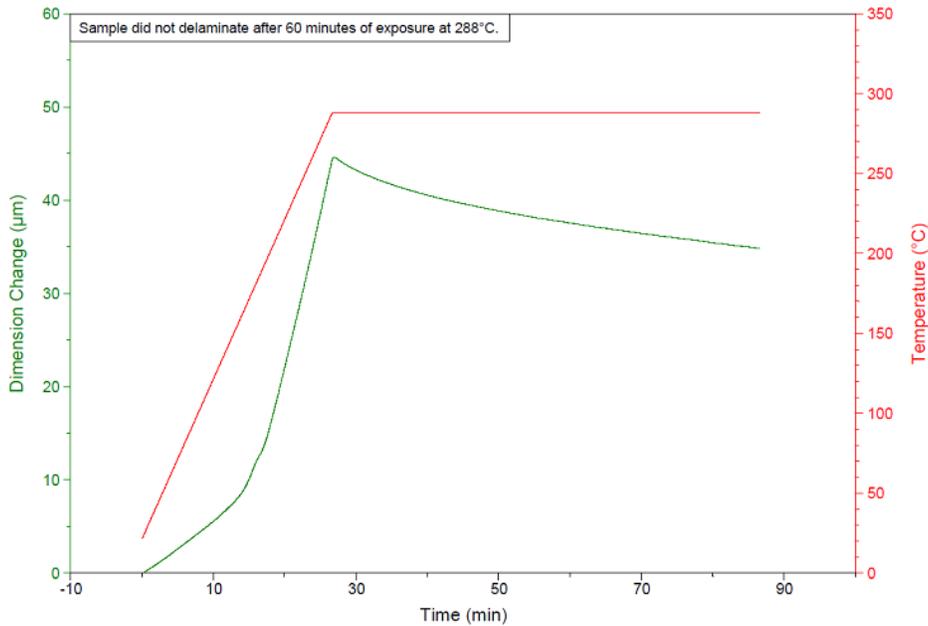
The thermal and physical properties of the laminate with a blend of PEN and CEN and with PEN only were similar, showing exceptional thermal stability with the onset of decomposition at above 410 °C. The CTE (Coefficient of Thermal Expansion) before Tg  $\alpha_1$  and after Tg  $\alpha_2$  were significantly lower for the laminate prepared with a blend of PEN and CEN. Figure 5 shows the TMA graph with CTE  $\alpha_1$  and  $\alpha_2$ .

In contrast to bifunctional DOPO-BPA, Material A is a multifunctional curing agent with average number of reactive groups of about 5-6. This allows a high degree of crosslinking, resulting in a high Tg. In addition, inherently high thermal stability of Material A and high cross-linking density results in unprecedented thermal stability of the cured epoxy, with the onset of decomposition at >400°C.

This high thermal stability is also improved as a result of the unique curing mechanism which leads to the formation of exceptionally stable bonds.



**Figure 4 - CTE  $\alpha_1$  and  $\alpha_2$  by TMA**



**Figure 5 - Time to delamination by TMA at 288 °C over 60 minutes**

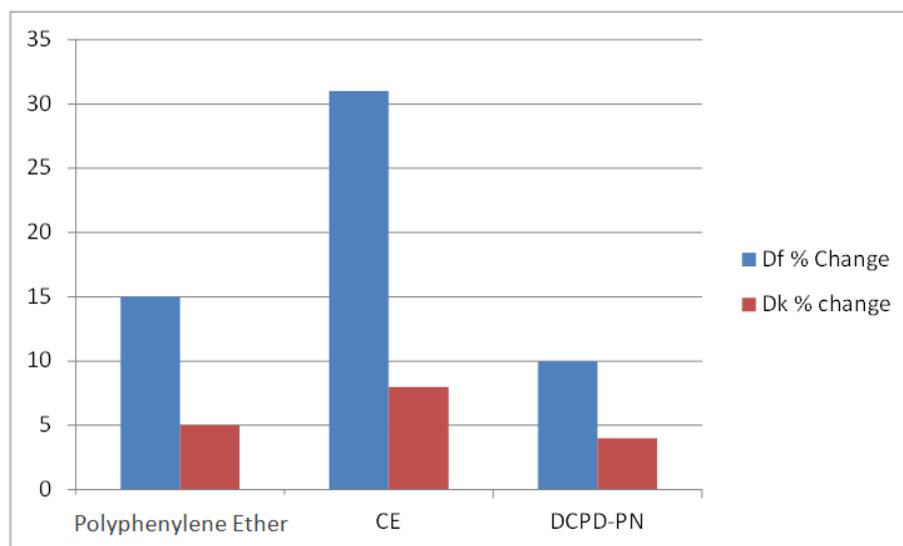
### Resin casts

In order to determine the Dk and Df of the cured composition, resin casts were prepared using the composition from Table 8 and similar curing conditions to those used in the laminate preparation. Permittivity and Loss Tangent were measured at 1GHz using the test procedure: IPC-TM-650, Method 2.5.5.9. In addition to the control sample, resin casts containing redistributed Polyphenylene Ether, Cyanate Ester (CE) and dicyclopentadiene (DCPD) Novolac were also prepared.

**Table 8 - Composition of prepared resin casts**

	Control	DCPD Novolac	CE	Polyphenylene Ether	Commercial Halogen-free System
CEN	29	28	28	25	35
PEN	24	23	23	20	28
Material A	38	37	35	36	
Material B					37
Phenolic Novolac	9.2	4.5		5.8	
DCPD Novolac		8.3			
CE			13		
Polyphenylene Ether				14	

Table 9 shows the T<sub>g</sub>, the onset of decomposition and the D<sub>k</sub> and D<sub>f</sub> of the resin casts, and Figure 6 shows the % change in the D<sub>k</sub> and D<sub>f</sub>. The CE had the strongest effect on both the D<sub>k</sub> and the D<sub>f</sub>, followed by Polyphenylene Ether. DCPD Novolac had the smallest effect in lowering both the D<sub>k</sub> and the D<sub>f</sub>. However, the level of DCPD Novolac was the lowest, so this effect may be more significant at a higher loading. Unfortunately, even with such a low loading, the T<sub>g</sub> of the cured sample was significantly reduced.

**Figure 6 - % change in the D<sub>k</sub> and D<sub>f</sub> with added Polyphenylene Ether, CE and DCPD Novolac**

With Polyphenylene Ether 14 wt%; BPA-cyanate (2,2-Bis(4-cyanatophenyl)propane) CE 13 wt%; DCPD-PN 8.3 wt% added in the formulations, respectively

**Table 9 - Tg, TGA, Dk and Df results for resin cast curing experiments**

	No additives	CE	Polyphenylene Ether	DCPD Novolac	Commercial Halogen-free System
Tg, °C	175	205	180	165	155
Onset of decomposition	<b>380</b>	<b>365</b>	<b>370</b>	<b>390</b>	<b>345</b>
Dielectric constant Dk (1 GHz)	3.26	3.01	3.10	3.13	3.19
Dielectric loss Df (1 GHz)	0.019	0.013	0.016	0.017	0.034

**Conclusions**

Material A is a reactive FR specifically designed for high performance laminates. It is a polymeric, phosphorus-based, multifunctional curing agent. The high degree of crosslinking when using Material A results in a high or very high Tg, depending on the formulation. In addition, this material is very thermally stable, even before cure. This, combined with a unique curing mechanism, results in highly thermally-stable laminates even when using simple epoxy Novolacs, with the onset of decomposition above 400 °C. Material A is suitable for high temperature applications. It enables the achievement of a V-0 rating in an unfilled epoxy system with a low, 2.5% P level. These properties, combined with low water-uptake; compatibility, with low Dk and Df resins and low CTE both before and after Tg, enable the use of Material A in a variety of applications.

# **New Phosphorus-based Curing Agents for PWB**

A. Piotrowski, M. Zhang, Y. Zilberman, Eran Gluz, S. Levchik  
ICL-IP America

# New Highly Efficient FR, Epoxy Curing Agent Material A

- Presentation outline
  - *Short summary of P flame retardants for PWB*
  - *Epoxy curing mechanism*
  - *Material A properties*
  - *Use of Material A in laminate preparation*
  - *Compatibility of Material A with low Dk resins/hardeners*
  - *Conclusions*

## Introduction

- PWB (Printed Wiring Boards) consist of reinforcing material and thermosetting resin
- Reinforcing material is usually E glass and thermosetting resin is epoxy cured with amine, phenolic or anhydride hardener
- Thermosetting resins like all organic polymers are flammable as a result of thermal decomposition producing flammable gasses
- All FR-4 (a glass-fiber reinforced epoxy laminates) have to meet defined flame retardancy standards.
- Flame retardants are used to allow passing of UL 94 flammability test.
- Either halogen-containing compounds or recently halogen-free flame-retardant compounds are used

## Introduction

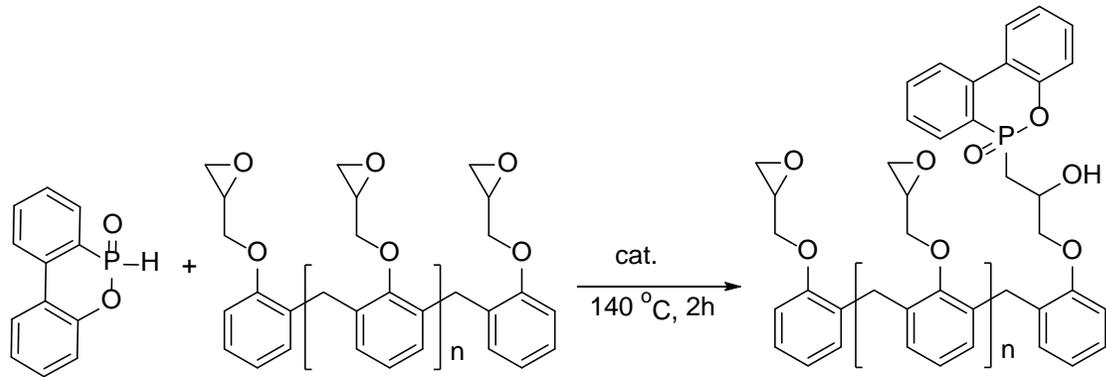
- Most flame retardants have a negative effect on many physical and electrical properties of PWB.
- The main challenge for flame retardants is finding materials that satisfy all of the electrical, thermal, chemical, and mechanical properties required for optimal device performance.
- Phosphorus based flame retardants are more efficient than Br based flame retardants.
- Br FR's have excellent hydrolytic stability and low water uptake, while this remains a challenge for many phosphorus based flame retardants.
- Reactive TBBA is a major flame retardant in PWB, we used similar approach and developed a reactive P based flame retardant Material A with high thermal and hydrolytic stability.

## Reactive flame retardant challenges

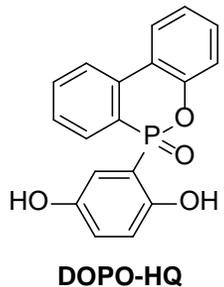
- Advantages
  - *No leaching into environment*
  - *Permanent*
  - *No blooming*
  - *No toxicity issue*
- Possible disadvantages
  - *Chemistry may have negative effect on  $D_k$ ,  $D_f$*
  - *Chemistry may have negative effect on  $T_g$ , thermal stability and water uptake*
  - *May limit ability to change formulation*
  - *Efficiency*

# Reactive flame retardant and Epoxy curing chemistry

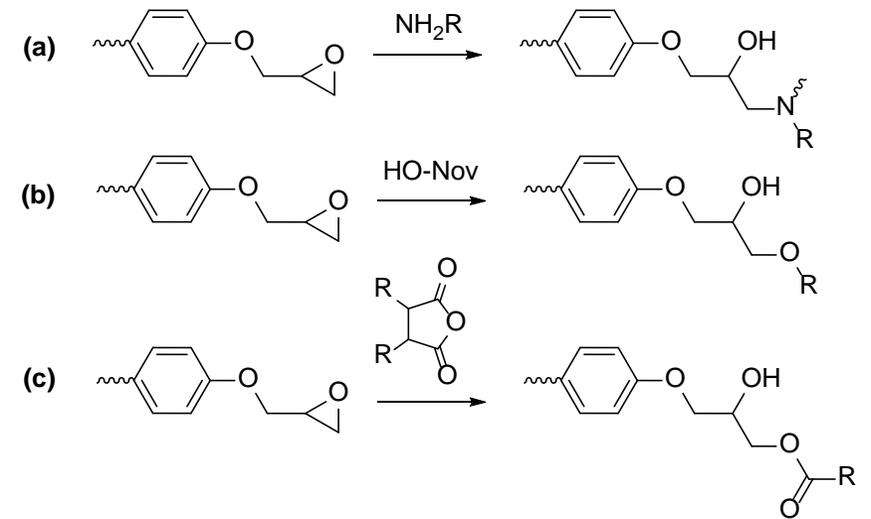
DOPO reaction with epoxy – reduced functionality



Preferred di-functional flame retardant



Epoxy curing chemistry



## Material A physical properties:

Property	Value
Appearance	Light brown flakes or off-white powder
Chemical nature	Polymer
Softening temperature, °C	>130
Phosphorus content	6.5-7%
T <sub>g</sub> , °C	100-110
Molecular weight, Mw	~1200
Thermal stability, TGA 5% wt. loss, °C	340-355
Solubility in MEK	>40%
Solubility in acetone	>40%
Viscosity of 60% MEK solution <sup>1</sup>	710 cp
Viscosity of 70% acetone solution	1900 cp
Varnish viscosity at 60% solids	220 cp
Reactive equivalent	220
Functionality	Multifunctional
FR efficiency unfilled system, V-0	2-2.5 wt.% P
Application with epoxy	Curing agent

<sup>1</sup> –very similar  
to Material B

## Prepreg

- Formulation - unfilled

24.0% CEN + 29.4% DEN + 35.3% Material A + 11.3 % PN + 0.07 phr AMI-2

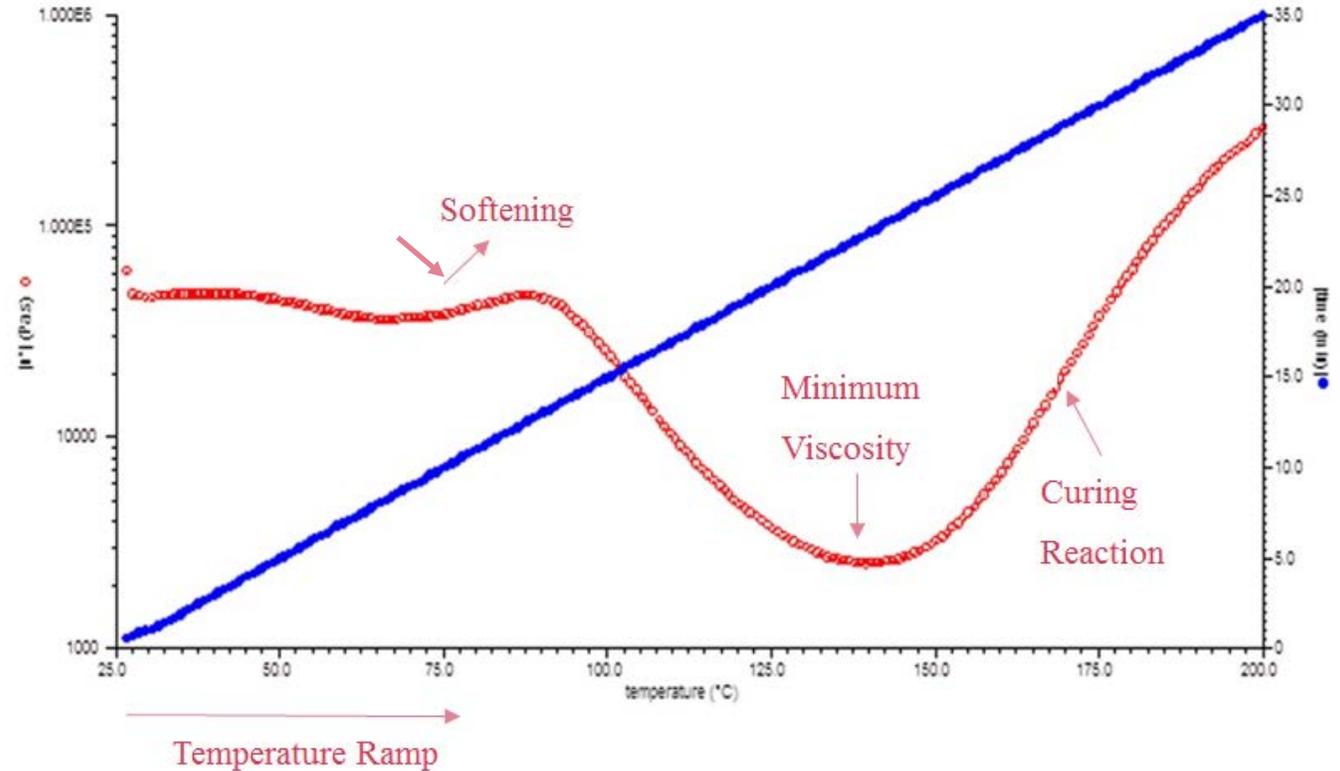
Prepreg Properties	Value
Resin content (wt %)	46
Varnish gel time (min, sec at 171°C)	320 sec
"B" staging at 165°C	210 sec
Flow (%)	>5
Prepreg gel time (min, sec at 171°C)	210 sec



Tack free even before B stage

# Lamination

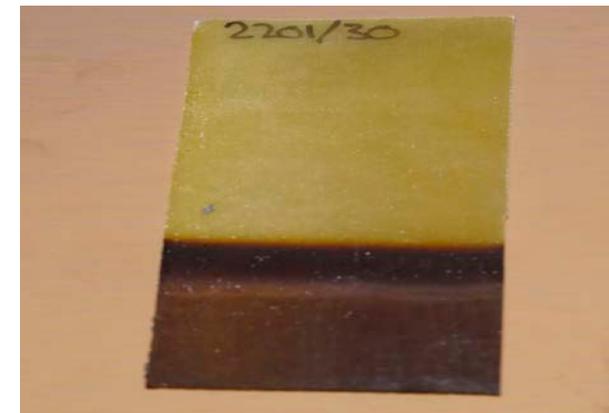
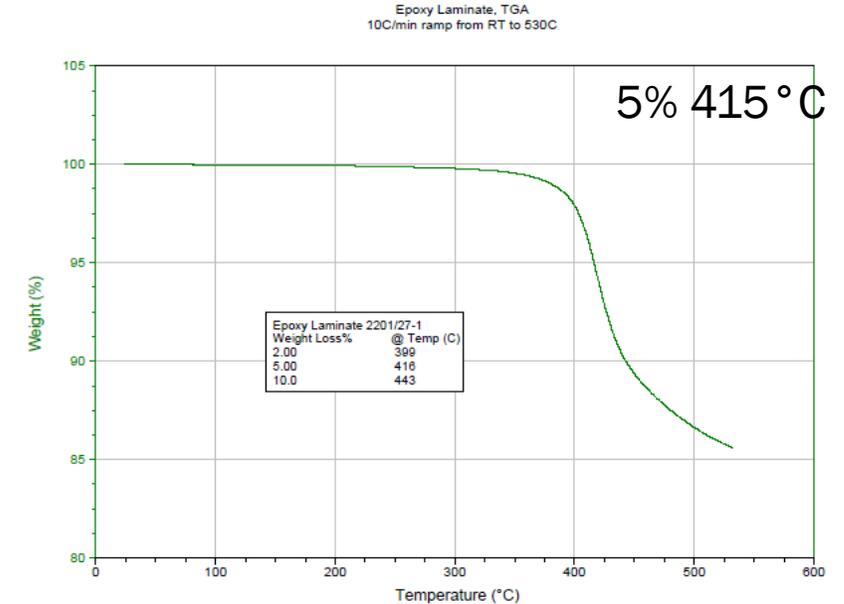
- Pressure cycle – 10 psi to 220 psi
- Final Pressure – 220 psi (or 15 Kg/cm<sup>2</sup>)
- Heating cycle – 25°C to 195°C (Ramp Rate – 10°C/min)
- Isothermal Heating – 195°C for 90 minutes



Complex viscosity profile of the prepreg at 5°C/min

## Thermal Stability

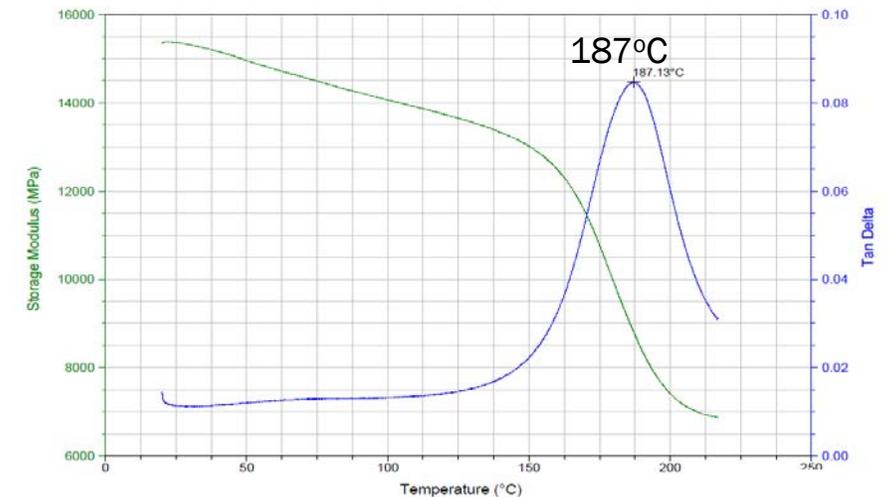
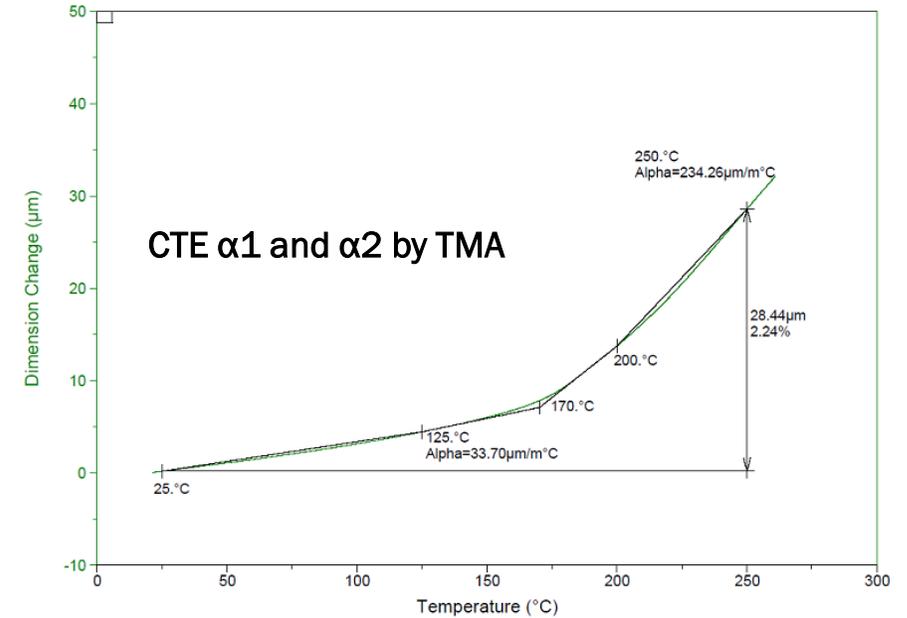
- Material A shows exceptional thermal stability
- Td 5%=415 °C for Material A
- High thermal stability is inherent property of Material A due to special curing mechanism
- No delamination in 60 min (T288 > 60 min)
- Good fit for high Tg application



120 min in T288 solder

## Glass Transition

- TMA, 2nd run
- $T_g = 170\text{ }^\circ\text{C}$
- $\text{CTE} = 35\text{ ppm} < T_g$
- $\text{CTE} = 235\text{ ppm} > T_g$
- Expansion 2.25% @ 25-250  $^\circ\text{C}$
  
- DMA
- $T_g = 180\text{-}190\text{ }^\circ\text{C}$



## Laminate properties for Material A formulations and Material B (commercial halogen-free system)

Formulation	Material A Formulation 1	Material A Formulation 2	Material B
Flammability <sup>1</sup>	V-0	V-0	V-0
Water absorption RT 24 hr <sup>2</sup>	0.06	0.07	0.2
PCT60 min water absorption % <sup>3</sup>	0.22	0.24	0.69
PCT120 min water absorption % <sup>3</sup>	0.36	0.38	
288°C PCT 60 min <sup>3</sup>	>20"	>10'	<10" failed
288°C PCT 120 min <sup>3</sup>	<10" failed	>10'	
Peel strength (pounds/inch of width) <sup>4</sup>	8.3	7.7	9.0
Tg DMA	192	183	175
Tg TMA	170		150
CTE ( $\alpha_1, \alpha_2$ ) <sup>5</sup>	33.7; 234.3	52.1; 307.2	
Td (5% wt. loss °C)	416	412	394
T288 min <sup>6</sup>	>60		>30

1) UL 94; 2) IPC-TM-650, Method 2.6.2.1; 3) Test procedure IPC-TM-650, Method 2.6.16

4) Test procedure IPC-TM-650; Method 2.4.8; 5) Test Procedure: IPC-TM-650, Method 2.4.25

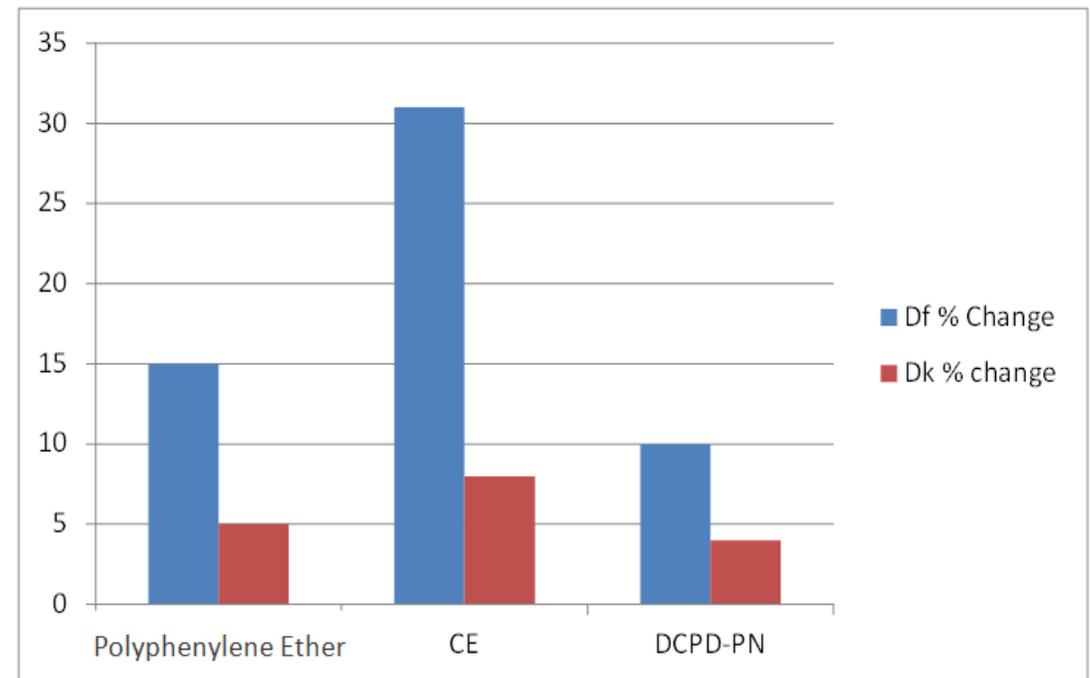
6) Test procedure IPC-TM-650, Method 2.4.24.1

## Resin Casts

Composition of prepared resin casts

Component	Formulation Name			
	Control	DCPD Novolac	CE	r-PPE
CEN/%	29	28	28	25
PEN /%	24	23	23	20
Material A/%	38	37	35	36
Phenolic Novolac /%	9.2	4.5		5.8
DCPD Novolac/%		8.3		
CE/%			13	
r-PPE %				14

% change in the Dk and Df with added r-Polyphenylene Ether (r-PPE), CE and DCPD Novolac



## Resin Casts

Tg, TGA, Dk and Df results for resin cast curing experiments

	Control	CE	r-PPE	DCPD Novolac	Material B
Tg, °C	175	206	180	163	155
Onset of decomposition	382	363	372	391	345
Dielectric constant Dk (1 GHz)	3.26	3.01	3.10	3.13	3.19
Dielectric loss Df (1 GHz)	0.019	0.013	0.016	0.017	0.034

## Sampling, Registration, IP

- Material A – is a developmental product.
- Available for sampling under NDA
- Material A is not registered
- Human and Environmental toxicity tests underway - initial results:

Study Name	Comments
Ames	Not mutagenic
Acute oral tox	Not toxic LD 50 >2000 mg/kg
Skin Irritation	Non-irritant to rabbit skin
Eye irritation	Mild irritant (=no classification is needed)
LLNA	Not skin sensitizer

- Material A meets REACH criteria for polymer – easier registration
- Patents are pending

## Conclusions

- Material A is a reactive FR specifically designed for high performance laminates, especially for high temperature applications.
- It is a polymeric, phosphorus-based, multifunctional curing agent.
- It provides high degree of crosslinking resulting in a high or very high T<sub>g</sub>.
- Material A is very thermally stable, even before cure. This, combined with a unique curing mechanism, results in highly thermally-stable laminates even when using simple epoxy Novolacs, with the onset of decomposition above 400°C.
- Material A enables the achievement of a solid V0 rating in an unfilled epoxy system with a low, 2.5% P level.
- These properties, combined with low water-uptake; compatibility, with low D<sub>k</sub> and D<sub>f</sub> resins and low CTE both before and after T<sub>g</sub>, enable the use of Material A in a variety of demanding applications.

**THANK YOU!**