Polyphenylene Ether Macromonomers. Iii. Enhancement of Dielectric Materials

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Abstract

Two major trends in printed wiring boards electronics are applications that require higher operating frequency, often in the radio frequency range (GHz), and the use of lead free solder assembly. Material requirements for dielectric materials have become more stringent. Key characteristics for dielectric materials are low dielectric constant, low dielectric loss, high use temperature, and low moisture uptake. The use of engineering thermoplastics has been investigated as a means to enhance performance of thermoset resins. In particular, polyphenylene ether (PPE) exhibits excellent hydrolytic stability, low moisture absorption, extremely high glass transition temperature, outstanding electrical properties over a wide temperature and frequency range, and ease of flame retarding without the use of halogenated materials. Investigations on the use of engineering thermoplastics in thermoset resins have pointed out the complexities of the network molecular architecture. Indeed, a wide variety of network morphologies were obtained within the fully cured material. PPE telechelic macromers have been reported as a breakthrough in the search for materials that broadly enhanced performance of dielectric materials. Thus the use of PPE macromonomers as a co-reactant in epoxy resins resulted in extensive performance advantages. Indeed, the use of PPE macromoners in epoxy resins resulted in single-phase networks, exhibited an increase in glass transition temperatures (T_g), lower dielectric properties, lower moisture absorption, and increased toughness. Single-phase matrices were also obtained with cyanate esters that exhibited lower moisture absorption and increased toughness. Vinyl modified PPE macromers were used in resins cured via radical polymerization. These resins exhibited very low moisture absorption in addition to high T_g and very low dielectric properties. The advantages of PPE macromoners in enhancing key properties of various dielectric materials suggest utility in a variety of demanding electronic packaging applications.

Introduction

Polyphenylene ether (PPE) is an amorphous, engineering thermoplastic, which is used extensively in blends and alloys. The chemical structure is depicted in Figure 1.

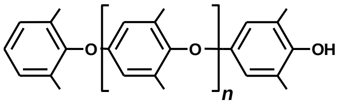
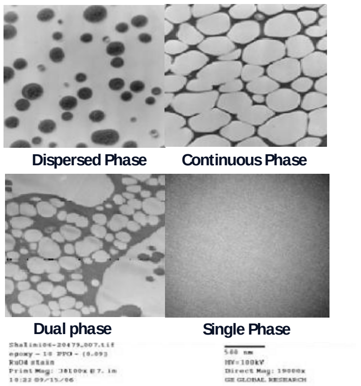


Figure 1. Chemical structure of PPE

This highly aromatic structure with a fairly stiff backbone contains no hydrolyzable bonds and no polarizable groups. These structural details result in a polymer with outstanding hydrolytic stability, very low moisture absorption, extremely high T_g (215°C; 419°F), outstanding dielectric properties over a wide temperature range, and low density relative to other engineering thermoplastics [1-3]. This unique performance profile would suggest that PPE would be an ideal material for electronic applications. There have been numerous studies on the use of PPE and other engineering thermoplastics in thermoset resins to boost their performance [4], however, the complexities of different morphologies, increases in viscosity, solubility issues, and variation in performance have hindered their successful application in electronic materials [5-7]. Indeed, the thermoplastic can be a dispersed phase, a continuous phase, or a co-continuous phase with the thermoset resin, [8]. Moreover, a variety of different morphologies can be obtained within the same cured part [4, 8]. In addition, the morphology can be varied by differences in the processing temperatures [9, 10]. In order to circumvent the limitation encountered in previous work in this area, unique low molecular weight PPE telechelic oligomers have been developed. These PPE macromonomers were tailored with functionality to react into epoxy resins and cyanate esters using condensation chemistry or with unsaturated monomers via a free-radical mechanism. [11] They exhibit very high solubility in solvents and monomers, and exhibit single-phase morphology in the final, fully cured material.

A comparison of the single-phase morphology of PPE telechelic oligomer in epoxy resin with some of the various two-phase morphologies that can be obtained in epoxy resins are shown in the TEM (transmission electron microscopy) pictures in Figure 2. The PPE appears as dark regions in these RuO_4 stained samples.



Dispersed Phase Continuous Phase

Dual phase Single Phase

Figure 2. Microstructure of various PPE/Epoxy resins

Materials

The PPE-M telechelic oligomer is under development by Sabic Innovative Plastics under the MX90 developmental designation (commercial designation Noryl® SA90 trade name). This hydroxyl-terminated oligomer is designed for use with epoxy resins and cyanate ester resins. The structure of PPE-M is depicted in Figure 3 and properties appear in Table 1.

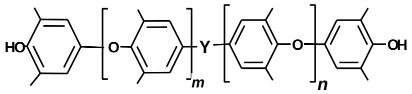


Figure 3. Structure of PPE-M

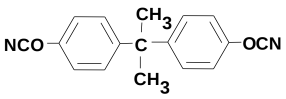
Table 1. Typical Properties of PPE-M

PROPERTY	VALUE
Hydroxyl equivalent weight	800 g/mol
Number average molecular weight	1700
Weight average molecular weight	4200
Glass Transition Temperature	150°C
Solubility in MEK (25°C)	>50wt%
Solubility in toluene (25°C)	>50wt%

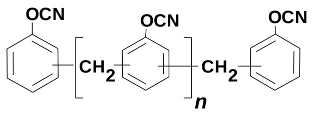
The epoxy resins used in the experiments were DGEBPA, bisphenol-A diglycidyl ether, (available as D.E.R.™ 332 from the Dow Chemical Company; epoxy equivalent weight of 170 g/eq.); and brominated bisphenol-A diglycidyl ether, (available as D.E.R.™ 560 from the Dow Chemical Company). Aluminum acetylacetonate (4 wt%) was used as the catalyst to cure castings of epoxy formulations. For laminates 2-ethyl-4-methyl imidazole (0.3-1.0 phr) was used as the catalyst.

Multifunctional epoxy resins were supplied by Hexion Specialty Chemicals (cresol novolac epoxy, bisphenol A novolac epoxy, and tetraglycidyl ether of tetraphenolethane under the Epon® 164, Epon® SU-8, and Epon® 1031 trade names, respectively); and by CVC Specialty Chemicals (epoxidized meta-xylenediamine under Erisys® GA-240 trade name).

The phenol novolac (PN) was supplied by Georgia-Pacific Resins, Inc under the GP® 5833 trademark. The bisphenol A cyanate ester (BPA-CE) and the phenol novolac cyanate esters (PN-CE) were supplied by Lonza Group Ltd. under the PRIMASET® BADCy and PRIMASET® PT-30 trade names, respectively.



BPA-CE



PN-CE

Evaluation In Epoxy Resins

The examination of the performance of neat resins provides a unique window to observe the quantifiable effect of PPE telechelic oligomers incorporated into the epoxy network, unfettered by confounding factors such as fillers or reinforcement materials. Hence, castings were prepared with varying levels of PPE-M reacted with DEGBPA. The T_gs are increased with increasing levels of PPE telechelic oligomers as shown in Figure 4.

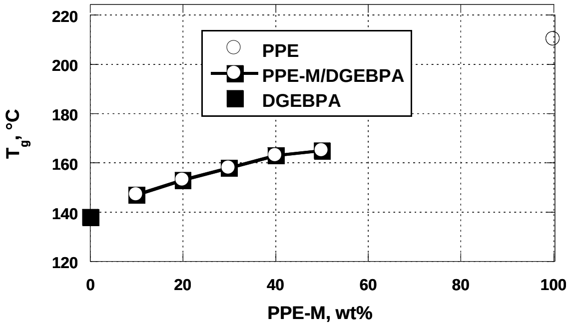


Figure 4. Effect of PPE-M on T_g of DGEBPA

PPE has excellent dielectric properties and the addition of PPE-M to DEGBPA results in decreases in dielectric constants (Relative Permittivity, Dk) and dissipation factors (loss tangent, Df). Figures 5 and 6 show the decrease in Dk and Df of DEGBPA as the amount of PPE-M is increased.

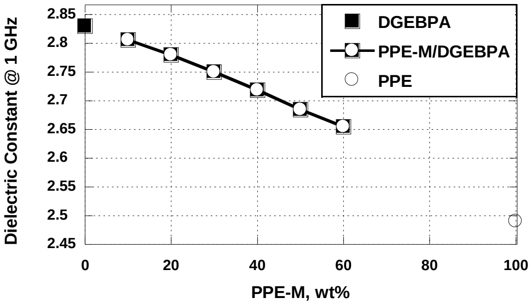


Figure 5. Effect of PPE-M on the Dielectric Constant of DGEBPA

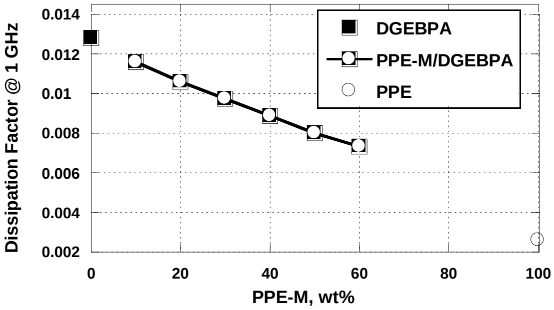


Figure 6. Effect of PPE-M on the Loss Tangent of DGEBPA

The toughness of DGEBPA castings is increased with the incorporation of PPE-M. The effect of PPE-M on the fracture toughness (K_{1C}) of DEGBPA is shown in Figure 7. The fracture toughness increases with increasing PPE-M content.

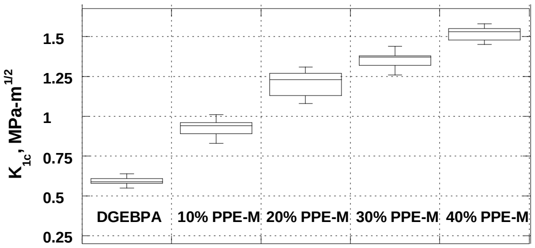


Figure 7. Effect of PPE-M on Fracture Toughness of DGEBPA

PPE does not contain polar groups which would strongly hydrogen bond to water molecules, and correspondingly, has very low water absorption. The water absorption of DGEBPA after immersion in water is reduced by the addition of PPE telechelic oligomers. Since water has high dielectric properties, lower moisture absorption would be desirable for reducing end-use performance variability. Water uptake was determined by immersion in water at ambient temperatures and the results appear in Figure 8.

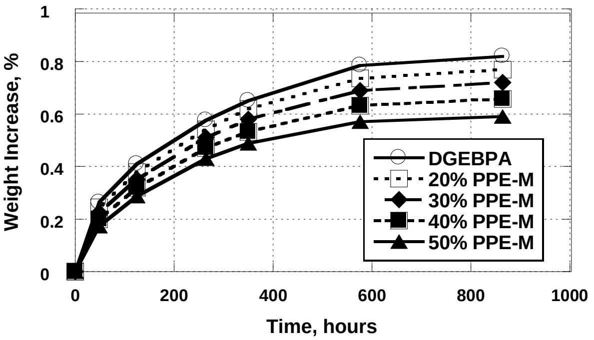


Figure 8. Effect of PPE-M on water uptake of DGEBPA

Clearly, the increase in T_g, lower dielectric properties and lower moisture absorption suggest that PPE-M offers a viable option for enhancing the performance of epoxy based dielectric materials.

Comparison With Novolac Resins

Novolac resins are utilized as hardeners for epoxy resins in order to increase the T_g. Indeed, it is reported that novolac/epoxy resins are used extensively to produce encapsulated semiconductors, and discrete devises as transistors, capacitors, diodes, rectifiers, and resistors. [12, 13]

A comparison of phenol novolac resins (PN) versus PPE-M on the effect of properties of DGEBPA was studied. Castings were prepared where the amount of PN used was chosen at 38wt% because it is close to the recommended stoichiometric amount of epoxy and hydroxyl groups (from the PN). For comparative purposes, the amount of PPE-M used in this study was also 38wt%.

Properties from castings appear in Figures 9 and 10. In Figure 9, both the PN and PPE-M increase the T_g over DGEBPA by itself. However, the PPE-M is more effective in increasing the T_g at an equal weight basis.

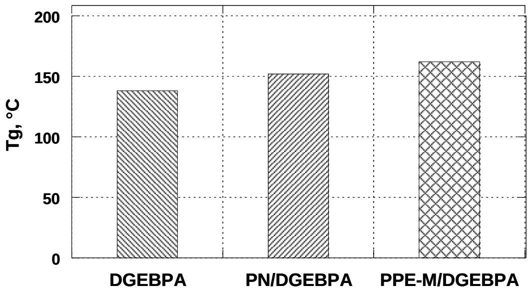


Figure 9. Effect of PN and PPE-M on Glass Transition Temperature

Pendulum impact results in Figure 10 shows that the impact strength of DGEBPA was increased 70 and 125% by PN and PPE-M, respectively.

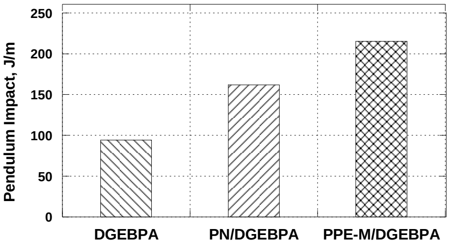


Figure 10. Effect of PN and PPE-M on Pendulum Impact

The dielectric properties of polymers are a function of several variables including water absorption. Indeed, the insulating properties of dielectric materials are reduced by water because water molecules have a dipole moment and are polarizable. [14] Resins containing polar moieties are more susceptible to moisture absorption because water molecules can hydrogen bond to these polar moieties. [15, 16]

A comparison of the moisture uptake and dielectric properties were examined by immersion of test specimens in water at 80°C. The resins were DGEBPA, PPE-M/DGEBPA, and PN/DGEBPA. The higher temperature was chosen to accelerate the water absorption. The results appear graphically in Figures 11 and 12. For all the materials, the dielectric constants, loss tangents and moisture uptake increase with longer immersion times. Compared to DGEBPA, the PN increases the moisture absorption and dielectric properties. Where as, the PPE-M decreases the moisture uptake and dielectric properties. The increases are much less for the networks prepared from PPE-M.

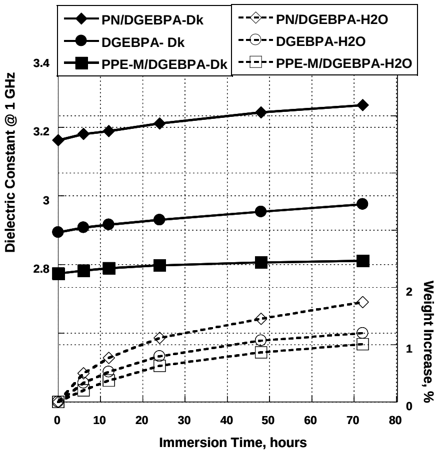


Figure 11. Effect of Moisture Absorption on Dielectric Constant

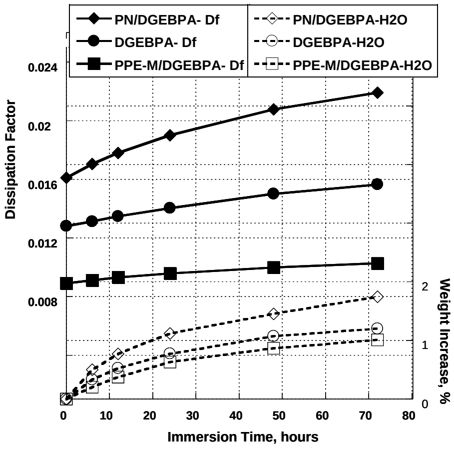


Figure 12. Effect of Moisture Absorption on Loss Tangent

Clearly, the use of PPE-M in epoxy resins exhibits performance advantages over novolac hardeners in the area of T_g, impact strength, and retention of dielectric properties under moist conditions.

Epoxy Laminates

Laminates were prepared with PPE-M, multifunctional epoxy resins, and 7628-E glass cloth with 627 finish (from BGF Industries). A summary of their properties appears in Table 2.

Table 2. Properties of PPE-M/Epoxy Laminates

FORMULATION	FR-4	A	B	C	D
PPE-M, wt%	FR-4	50	50	50	50
Brominated BPA epoxy, wt%		25	25	25	25
Cresol novolac epoxy, wt%		25	-	-	-
BPA novolac epoxy, wt%		-	25	-	-
Epoxidized meta-Xylenediamine, wt%		-	-	25	-
Tetraglycidyl ether of tetraphenolethane, wt%		-	-	-	25
2-ethyl-4-methyl imidazole, phr		0.3	1	0.3	1
Thickness, mm	-	1.988	2.074	1.853	1.999
Glass fiber content, %	~50	53.1	47.1	51.7	48.3
Tg (DSC), °C	140-150	190	185	175	193
Time to Delamination (288°C), min.	-	>30	>30	>30	>30
Dielectric Constant					
@ 100 MHz	-	4.120	3.929	3.936	3.907
@ 500 MHz	-	3.932	3.797	3.785	3.805
@ 1 GHz	4.4	3.614	3.575	3.505	3.633
Dissipation Factor					
@ 100 MHz	-	0.0147	0.0122	0.0126	0.0130
@ 500 MHz	-	0.0132	0.0106	0.0112	0.0115
@ 1 GHz	0.015	0.0124	0.0111	0.0101	0.0107
Flammability, UL94	V-0	V-0	V-0	V-0	V-0

Evaluation In Cyanate Esters

Cyanate esters are a family of monomers and oligomers, which contain the reactive ring-forming cyanate functional groups. Cured cyanate esters give highly crosslinked networks that exhibit very high T_gs, and low dielectric properties. [17] These highly crosslinked structures tend to have low toughness. The cyclotrimerization of cyanate groups form triazine ring units, which have a tendency to absorption moisture.

PPE-M will react with cyanate esters and become part of the three-dimensional triazine network. Based on the performance enhancements in epoxy resins, PPE-M was evaluated in cyanate esters. [18]

Castings were prepared containing 0, 10, 20, 30, 40, 50 wt% PPE-M in BPA-CE and PN-CE. Over the composition range studied, all cured resins were transparent and exhibited a single T_g as determined by differential scanning calorimetry (DSC). Both the BPA-CE and PN-CE when cured gave materials with a very high crosslink density and very high T_gs of 285 and 320°C, respectively. The addition of PPE-M to these CEs results in lower T_gs. This is probably the result of the lower T_g of PPE-M and a decrease in the crosslink density of the cured material. The results appear in Figure 13.However, all the T_gs of the CE networks remained above 220°C.

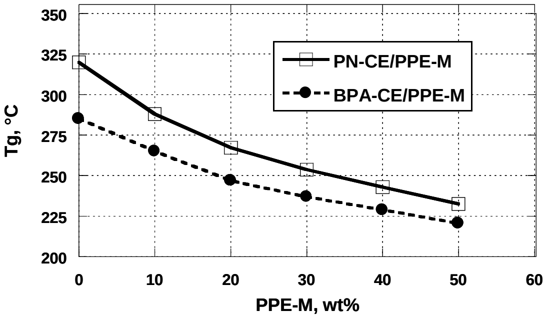


Figure 13. Effect of PE-M on Tg of BPA-CE and PN-CE Castings

CE based networks can have very high crosslink densities in which there are significant restriction the molecular motions of the groups between crosslink sites and can result in decreased toughness. Fracture toughness (K_{1C}) was used to study the effect of PPE-M on the toughness of CE networks. The data is summarized in Figure 14. The fracture toughness of BPA-CE and PN-CE based networks increases with PPE-M content.

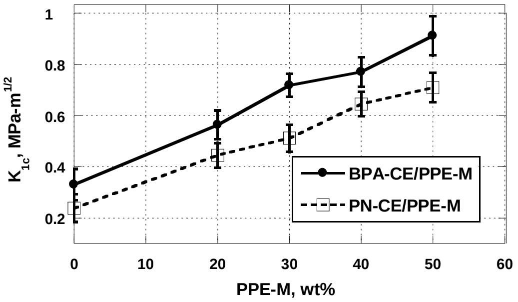


Figure 14. Effect of PE-M on Fracture Toughness of BPA-CE and PN-CE

A unique feature of CEs is their low dielectric properties. The effect of PPE-M on dielectric properties of BPA-CE based networks was evaluated. The results appear in Figures 15 and 16. Over the composition and frequency ranges studied, all networks exhibited very low dielectric properties. For the dissipation factor, there is a slight increase with increasing levels of PPE-M.

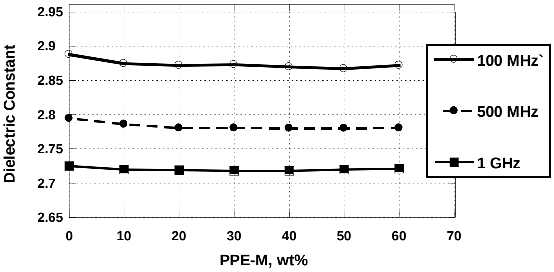


Figure 15. Dielectric Constants versus PPE-M Levels in BPA-CE

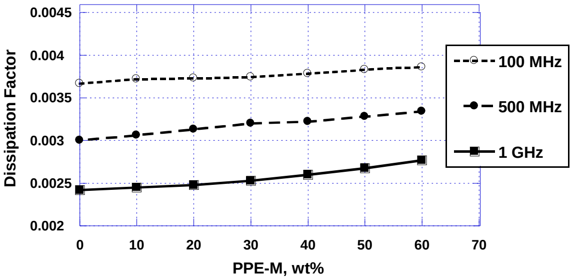


Figure 16. Loss Tangent versus PPE-M Levels in BPA-CE

Water molecules will hydrogen bond with triazine rings in cured CE resins. Hence, the high levels of triazine ring structures in cured cyanate ester resins results in absorption of water. This moisture absorption can have an adverse effect on dimensional stability and dielectric properties. Where as, the water absorption of PPE is very low.

Hence, a comparison of the moisture uptake and dielectric properties were examined for BPA-CE with 0, 25, and 50wt% PPE-M. The results from immersion of test specimens in water at 80°C on moisture absorption and dielectric properties appear in Figures 17 and 18. As the moisture absorption increases, both dielectric constants and dissipation factors increase. The incorporation of PPE-M into the CE matrix results in decreased moisture absorption and less change in dielectric properties commensurate with the level of PPE-M.

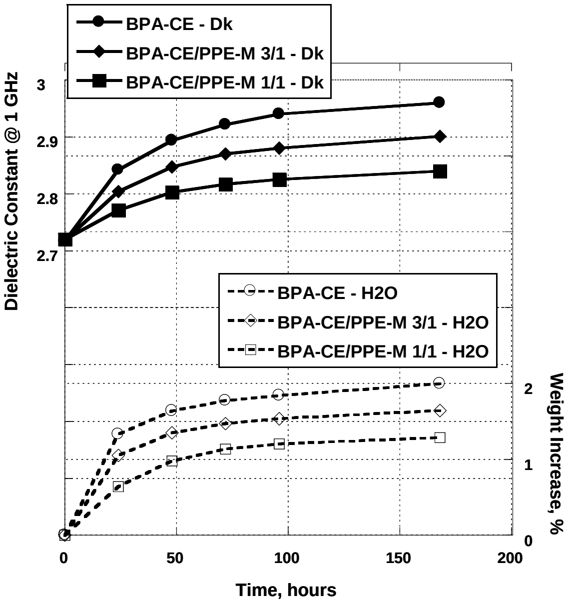


Figure 16. Effect of Moisture Absorption on Dielectric Constant of BPA-CE

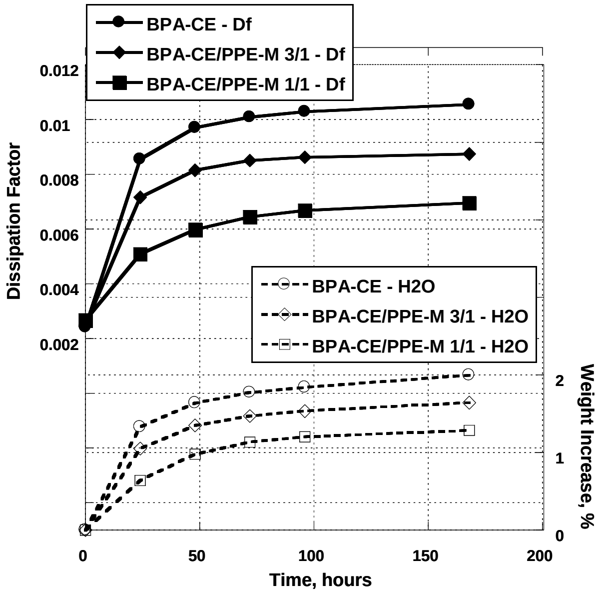


Figure 17. Effect of Moisture Absorption on Loss Tangent of BPA-CE

Laminates were prepared with PPE-M, BPA-CE, PN-CE, and 7628 style glass cloth. For the flame retardant formulation, tris(2,4,6-tribromophenoxy)-1,3,5-triazine (Brominated triazine) was used as the flame retardant. A summary of their properties appears in Table 3.

Table 3. Properties of PPE-M/CE Laminates

FORMULATION	Non-FR	FR
PPE-M	50	30
PN-CE	25	27.5
BPA-CE	25	27.5
Brominated triazine	-	15
Thickness, mm		
Glass fiber content, %	52.5	48.3
Tg (DSC), °C	215	232
Time to Delamination (288°C), min.	>30	>30
Dielectric Constant		
@ 100 MHz	3.500	3.557
@ 500 MHz	3.473	3.537
@ 1 GHz	3.425	3.515
Dissipation Factor		
@ 100 MHz	0.0035	0.0035
@ 500 MHz	0.0034	0.0034
@ 1 GHz	0.0033	0.0033
Flammability, UL94	-	V-O

Free Radical Cure Systems

For thermoset resins cured via free radical polymerization, the terminal OH end group of PPE-M was replaced with a methacrylate group. There are two important benefits of this change. First replacement of the aromatic hydroxyl which will act to quench free radicals and inhibit the polymerization [19, 20]. Secondly, the methacrylate group facilitates incorporating the PPE into the thermoset matrix [21, 22]. The generic structure the methacrylate of PPE-M (m-PPE-M) is shown in Figure 18.

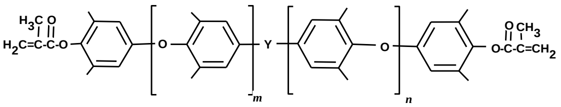


Figure 18. Structure of Methacrylate of PPE-M

Castings were made with triallyl isocyanurate (TAIC) resin and t-butyl styrene/divinyl benzene (TBS/DVB) resins. The resins were cured with 1.5 phr 2,5-dimethyl-2,5-di(t-butylperoxy)hexane. Properties appear in Table 4.

Table 4. Properties of TAIC and TBS/DVB based castings

FORMULATION	E	F
Methacrylated PPE-M	50	50
TBS	40	-
DVB	10	-
TAIC	-	50
Tg (DSC), °C	194	198
Dielectric Constant		
@ 1 GHz	2.55	2.75
@ 2.4 GHz	2.53	2.73
@ 10 GHz	2.52	2.71
Dissipation Factor		
@ 1 GHz	0.0038	0.0049
@ 2.4 GHz	0.0037	0.0048
@ 10 GHz	0.0036	0.0046

Moisture uptake was studied by immersion in water at 80C. For comparison, DGEBPA and TAIC resins were included in this study. The data appear in Figure 19.

TAIC shows very high water uptake because of its very high level of triazine rings. The addition of 50wt% m-PPE-M to TAIC (Formulation F) significantly decreases the water uptake. The TBS/DVB based resin (Formulation E) exhibited extremely low levels of moisture uptake. Both the TBS and DVB monomers are non-polar and have no sites for hydrogen bonding.

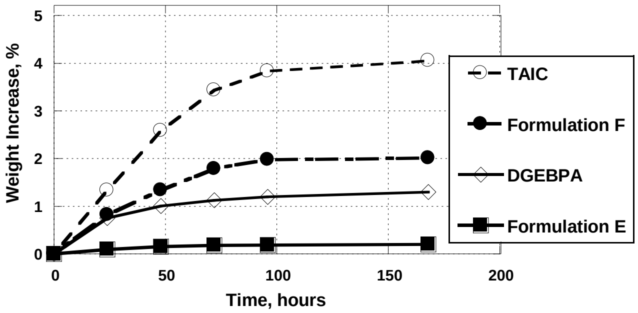


Figure 19. Moisture Uptake in TAIC and TBS/DVB Castings

The use of methacrylate of PPE-M in resins and monomers that cure by free radical polymerization offer a potential route to higher performance over epoxy based resin systems.

Conclusions

PPE-M telechelic oligomers were evaluated in epoxy and cyanate ester resins. The results suggest that PPE-M is an effective co-reactant in epoxy and cyanate ester resins and increases the toughness and lowers with moisture sensitivity. This lower moisture absorption results in less change in dielectric properties. Furthermore, in epoxy resins the PPE-M increases the T_gs and lowers the dielectric properties.

In cyanate ester resins, there was little change in dielectric properties over the composition and frequency ranges studied. The high T_gs of cyanate esters were decreased by the PPE-M. However even with 50wt% PPE-M the T_gs were above 220C.

The performance attributes of PPE-M suggest that they would be viable materials for use in dielectric materials for electrical and electronic components.

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POLYPHENYLENE ETHER MACROMONOMERS. III. ENHANCEMENT OF DIELECTRIC MATERIALS

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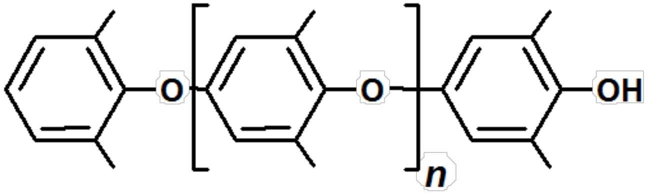
Selkirk, NY 12158

PPE

Poly(2,6-dimethyl-1,4-phenylene ether)



Used in blends of Engineering Thermoplastics

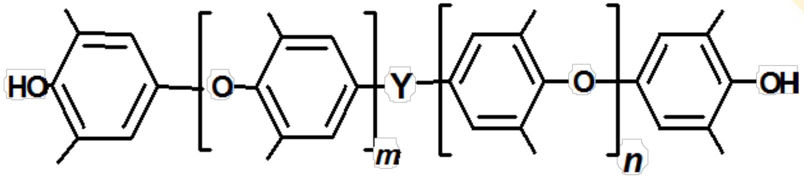
PPE FEATURES

- High temperature resistance (T_g = 215°C)
- Hydrolytically stable
- Low moisture uptake
- Excellent electrical properties
  - (over a wide temperature and frequency range)
- Inherent flame retardancy (non-halogen FR)
- Dimensionally stable

High molecular weight - not suitable for thermoset resins

PPE TELECHELIC MACROMONOMER (PPE-M)

Telechelic macromonomer - terminally functional, linear, large monomer



PPE-M

PPE-M FEATURES

- **High T_g**
- **Hydrolytically stable**
- **Low moisture uptake**
- **Excellent electrical properties**

PLUS

- Very low molecular weight
- **Highly soluble in solvents and co-reactants**
  - **>50 wt% in MEK or toluene @ 25°C**
- **Low solution viscosity**
- Low melt viscosity
- **Bi-functional for increase reactivity**

Developed for use in thermoset resins

ENGINEERING THERMOPLASTICS IN THERMOSET RESINS

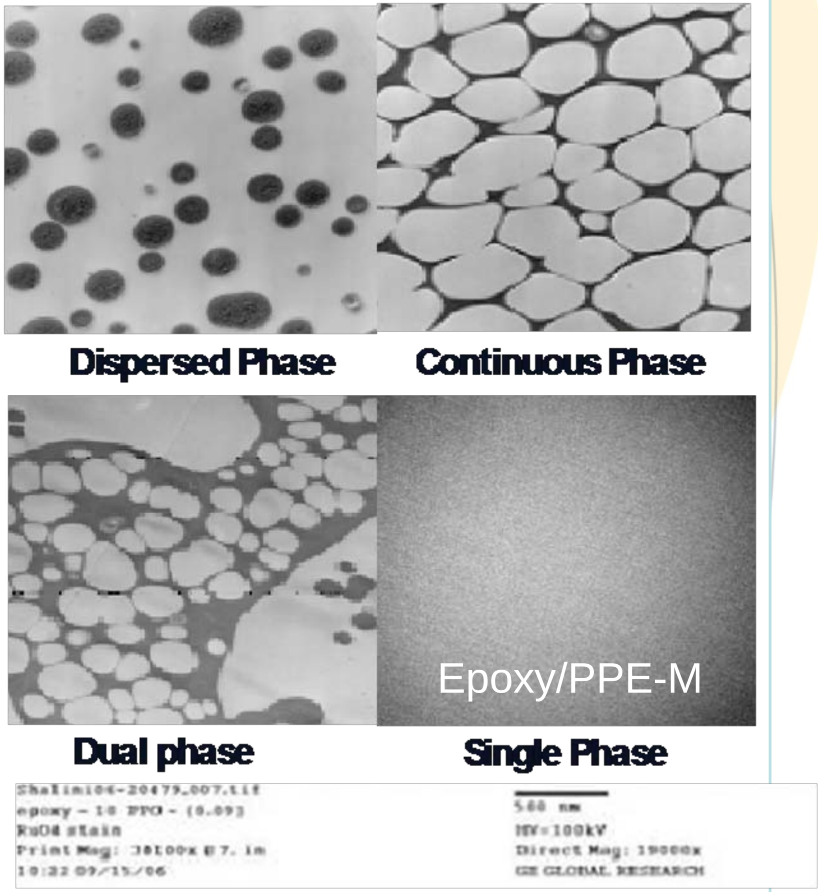
Use of engineering thermoplastics in thermoset resins

- Boost their performance
- Inherent limitations and sources of variability:
- **Properties are dominated by morphology**.
- A **variety of morphologies** can be obtain
- Morphology can **vary with** processing **temp.**

PPE-M gives stable, single-phase morphology

Morphology of Epoxy/PPE

RuO_4 stained; PPE = dark regions



Dispersed Phase

Continuous Phase

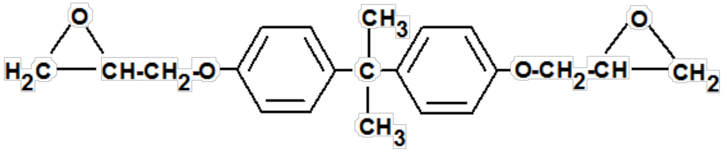
Dual phase

Single Phase

EVALUATION of PPE-M in EPOXY RESINS

Evaluation in castings

- Resin only - no glass fiber or filler
- Unfettered by confounding factors from fillers or reinforcement materials



Epoxy = diglycidyl ether of bisphenol A (DGEBPA)

Resins	Mn, g/mole	EEW, g/eq.	HEW, g/eq.	Tg, °C	Functionality
DGEBPA	~344	172	-	-	2
PPE-M	~1700	-	800	150	2

PPE-M dissolved in DGEBPA (~80°C)

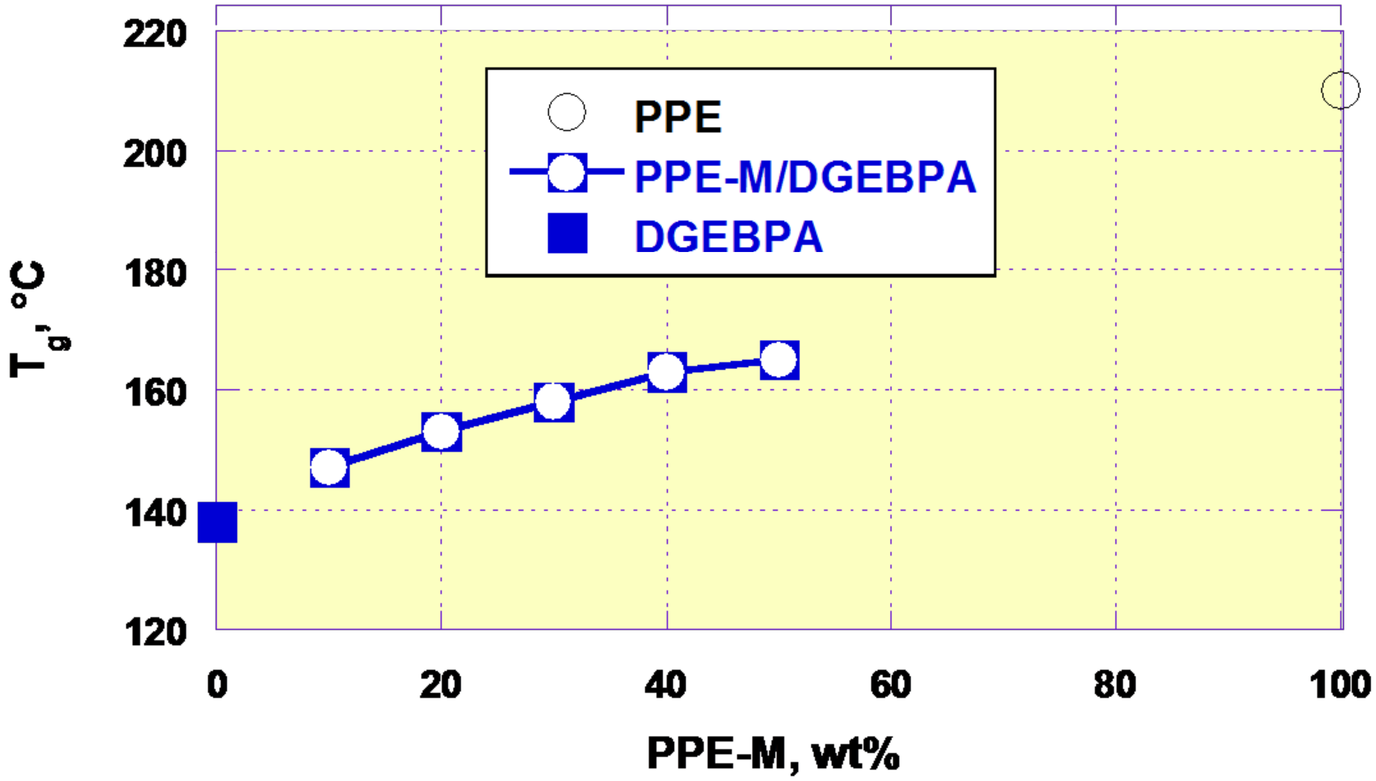
Cured using aluminum acetyl acetonate catalyst

1/8” (3.18mm) thick castings prepared. Test parts cut from castings.

PPE-M/DGEBPA sample designations

EFFECT of PPE-M on T_g of DGEBPA

Glass transition temperatures determined by DSC @ 20°C/min

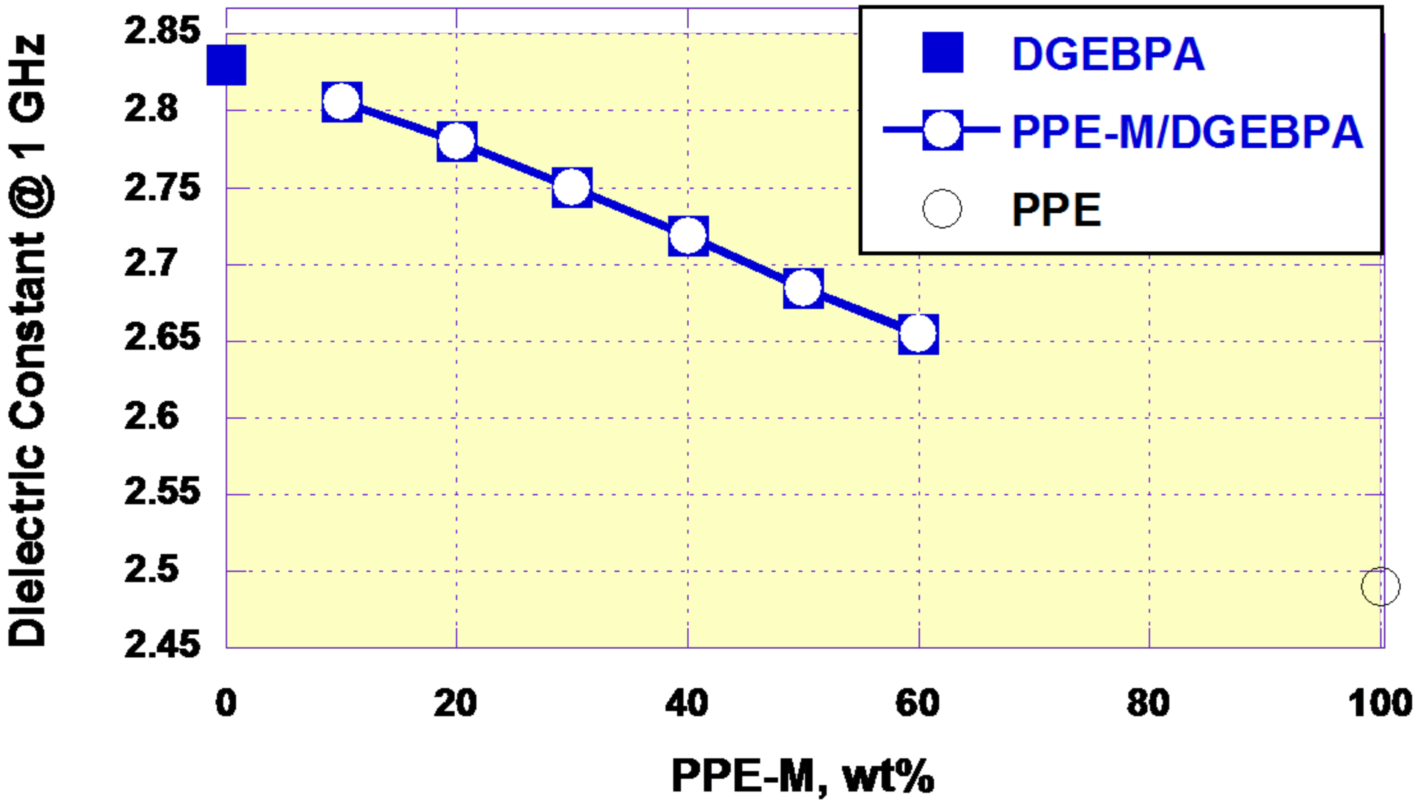


T_g increases with PPE-M levels

EFFECT of PPE-M on DIELECTRIC CONSTANT (D_k)

of DGEBPA RESIN

Measured using parallel plate technique

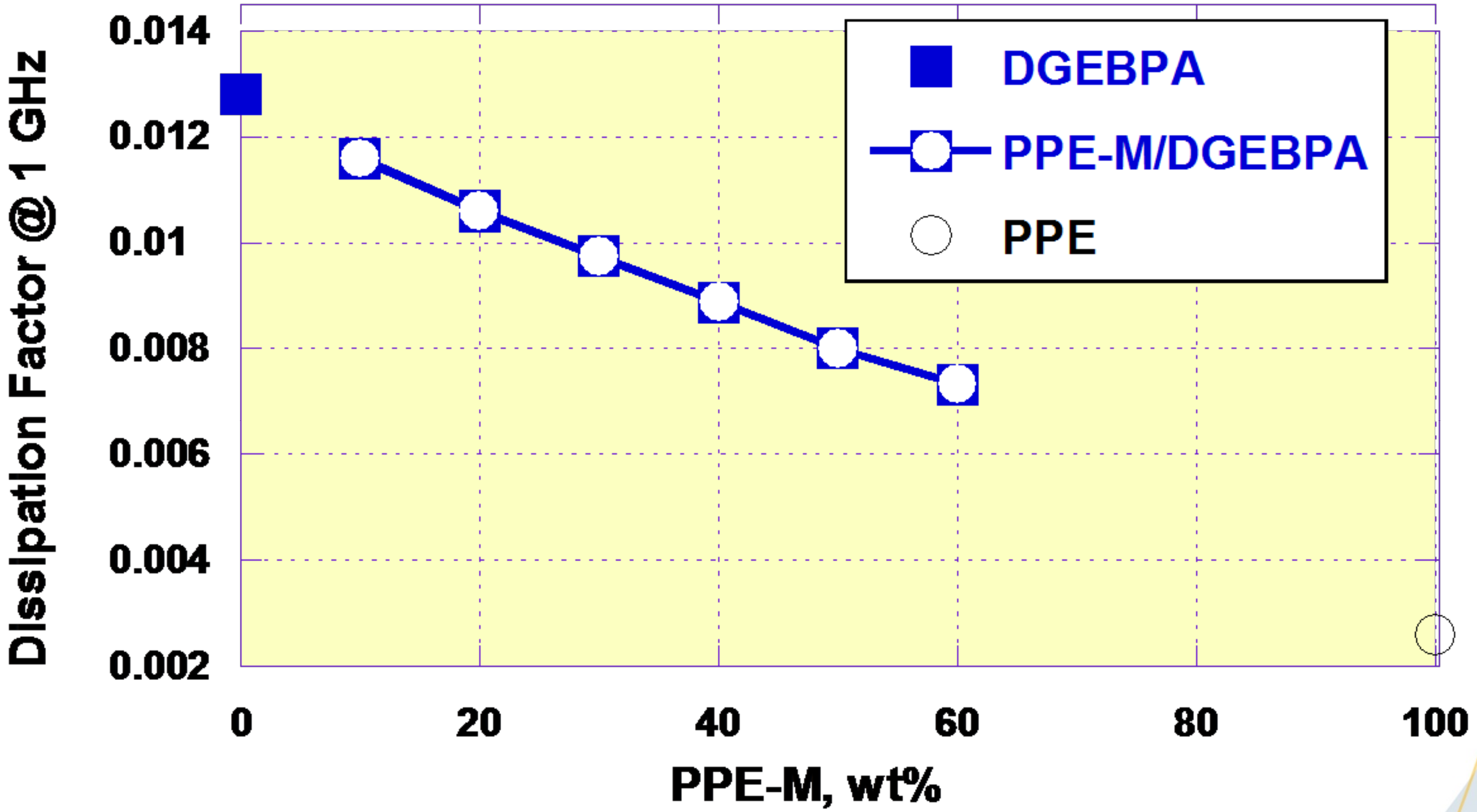


D_k decreases with PPE-M levels

EFFECT of PPE-M on DISSIPATION FACTOR (D_f)

of DGEBPA RESIN

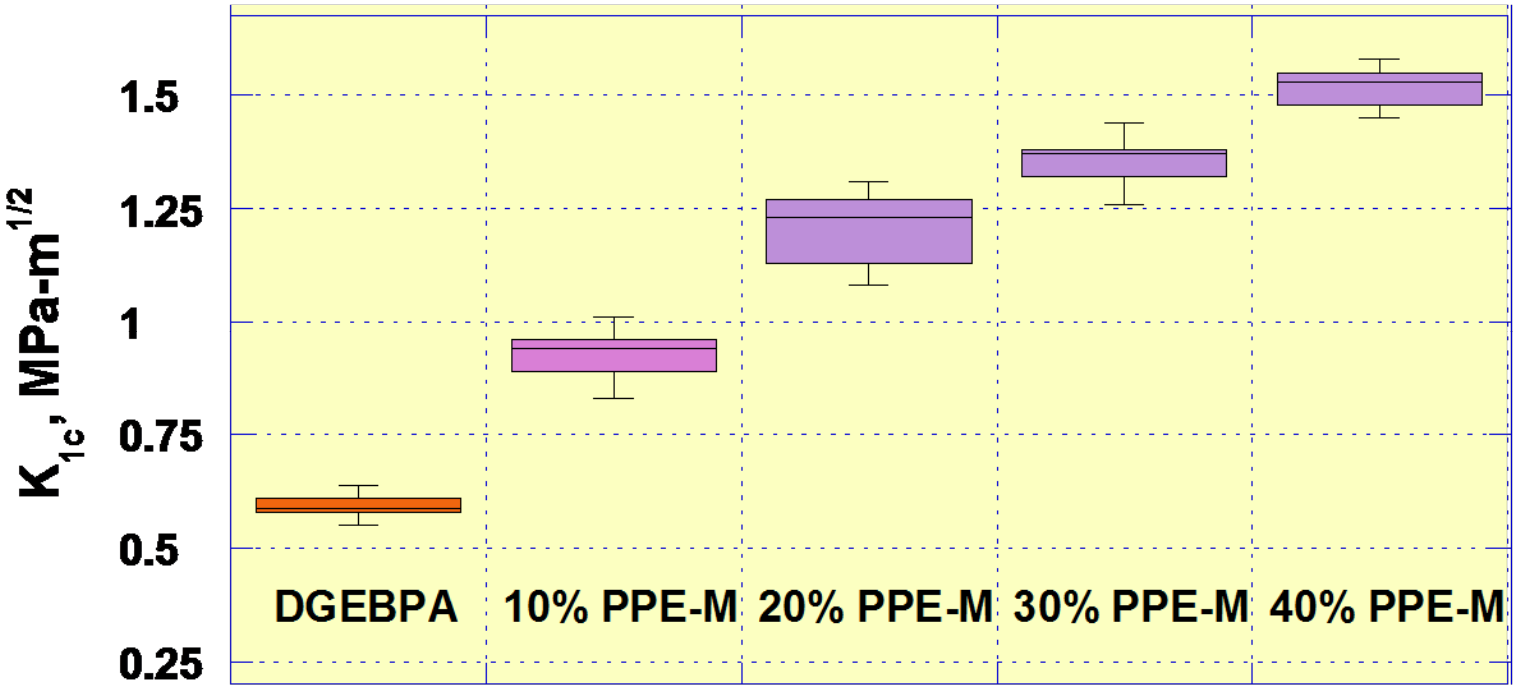
Measured using parallel plate technique



D_f decreases with PPE-M levels

EFFECT of PPE-M on FRACTURE TOUGHNESS

of DGEBPA RESIN

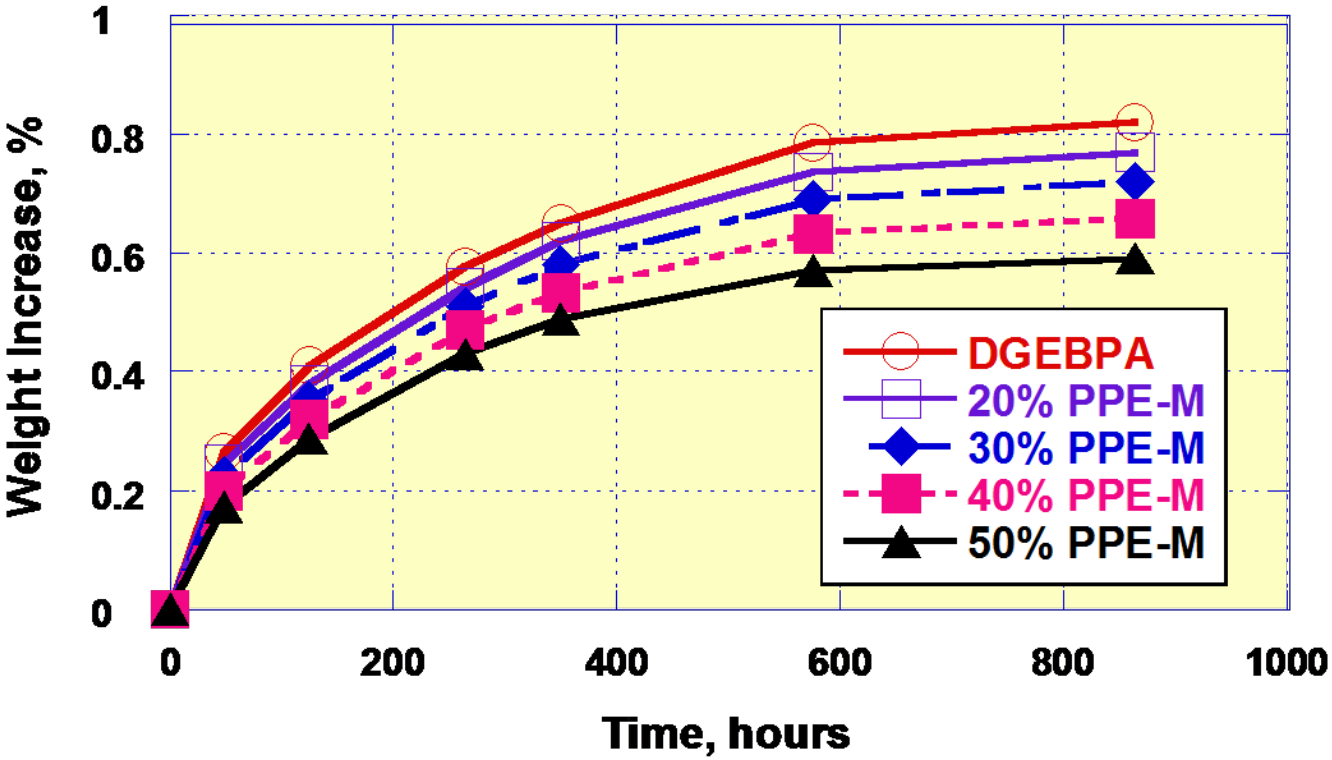


Toughness increases with PPE-M levels

EFFECT of PPE-M on MOISTURE ABSORPTION

of DGEBPA RESIN

Moisture uptake: Sample immersion in water at ambient temperature



Low H_2O uptake is important for stable dielectric properties

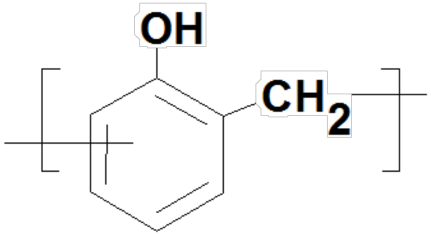
Water: Dk = 77.5; Df @ 100 MHz = 0.005, @ 3 GHz = 0.157

H_2O uptake decreases with PPE-M levels

COMPARISON of PPE-M with PHENOL NOVOLAC RESIN

in BPA EPOXY RESIN

Phenol novolac (PN) resins are used as hardeners in epoxy resin to increase T_g



PN

Comparison with PPE-M

38wt% in DGEBPA (~stoichiometric amount for PN)

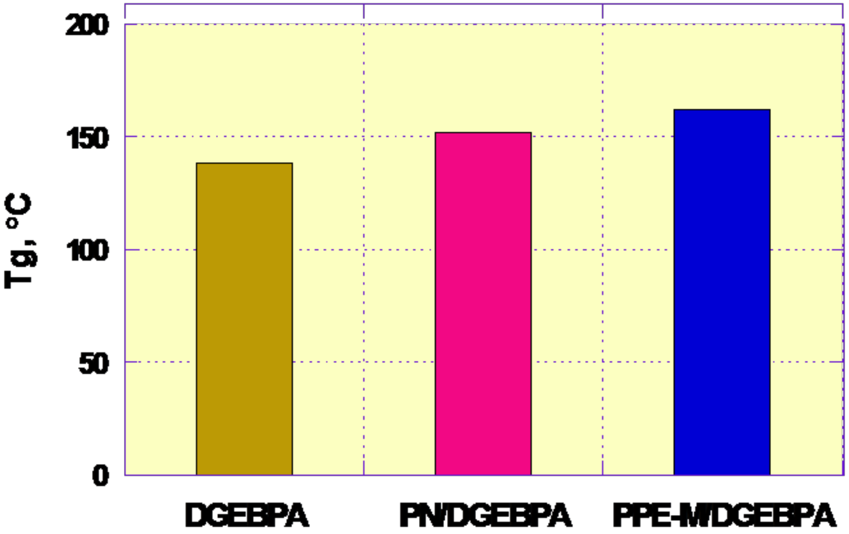
Resins	Mn, g/mole	EEW, g/eq.	HEW, g/eq.	Tg, °C	Functionality
DGEBPA	~344	172	-	-	2
PN	~1100	-	104	52	~10
PPE-M	~1700	-	800	150	2

Castings prepared for evaluation

COMPARISON of PPE-M and PN

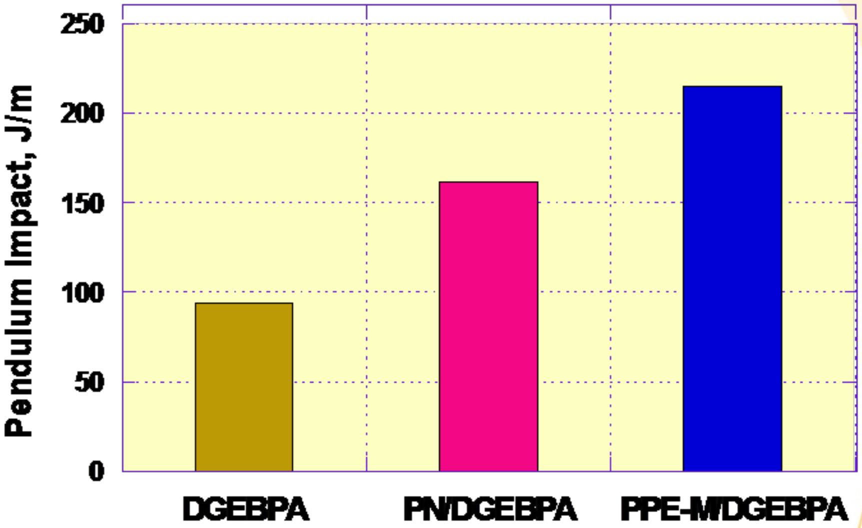
in BPA EPOXY RESIN

Effect on T_g



Determined by DSC @ 20°C/min

Effect on Impact Strength

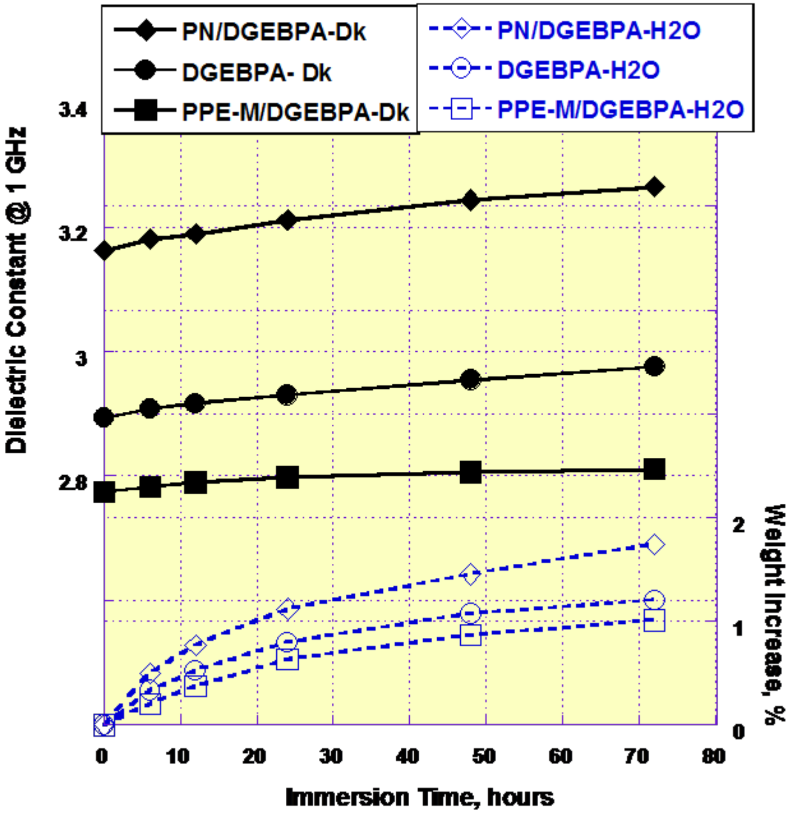


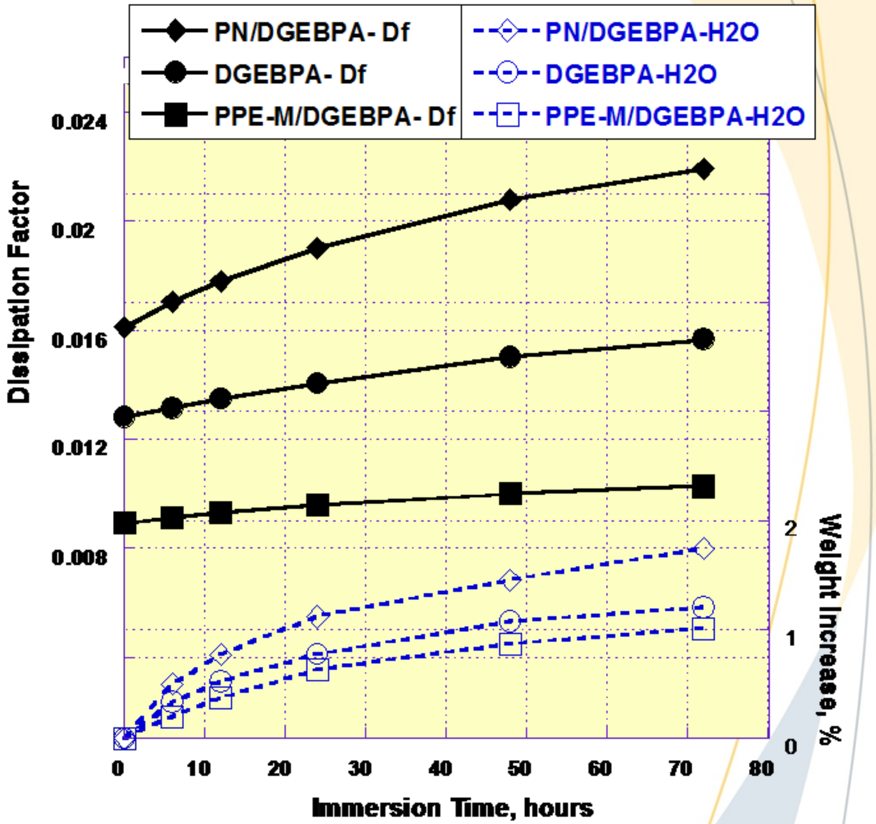
- PPE-M and PN increase T_g and Impact Strength
- PPE-M is more effective than PN

COMPARISON of PPE-M and PN

Effect of moisture uptake on dielectric properties

Effect of Moisture: Samples conditioned by immersion in water at 80°C

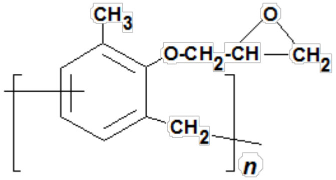


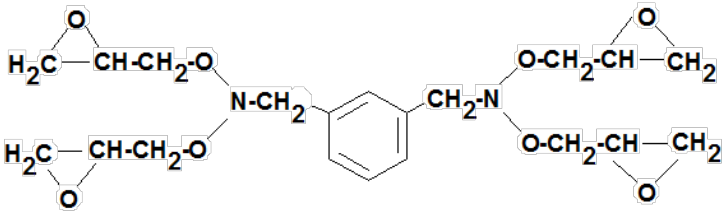


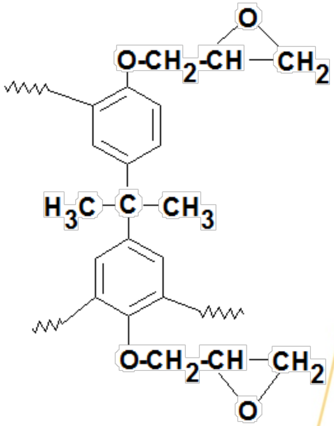
- PPE-M decreases H_2O uptake
- PN increases H_2O uptake
- PPE-M gives less change in dielectric properties

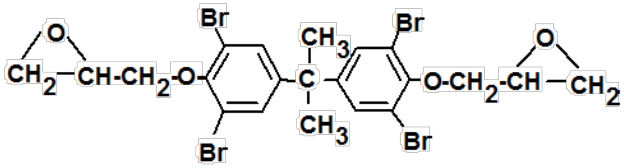
EPOXY LAMINATES

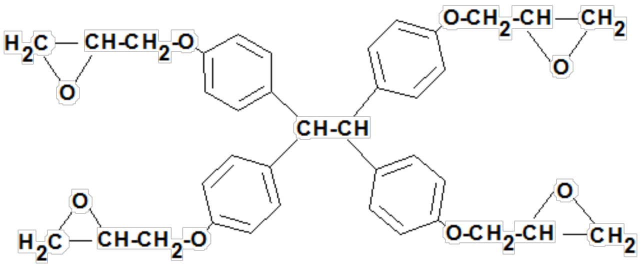
- PPE-M/DGEBPA laminates have T_g ~160-167°C
- Brominated BPA epoxy for flame retardance
- For higher T_g laminates, used multifunctional epoxy resin
- Glass cloth: E-glass, 7628 style with 627 finish

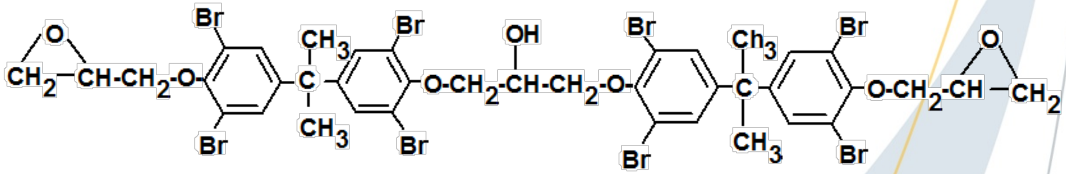






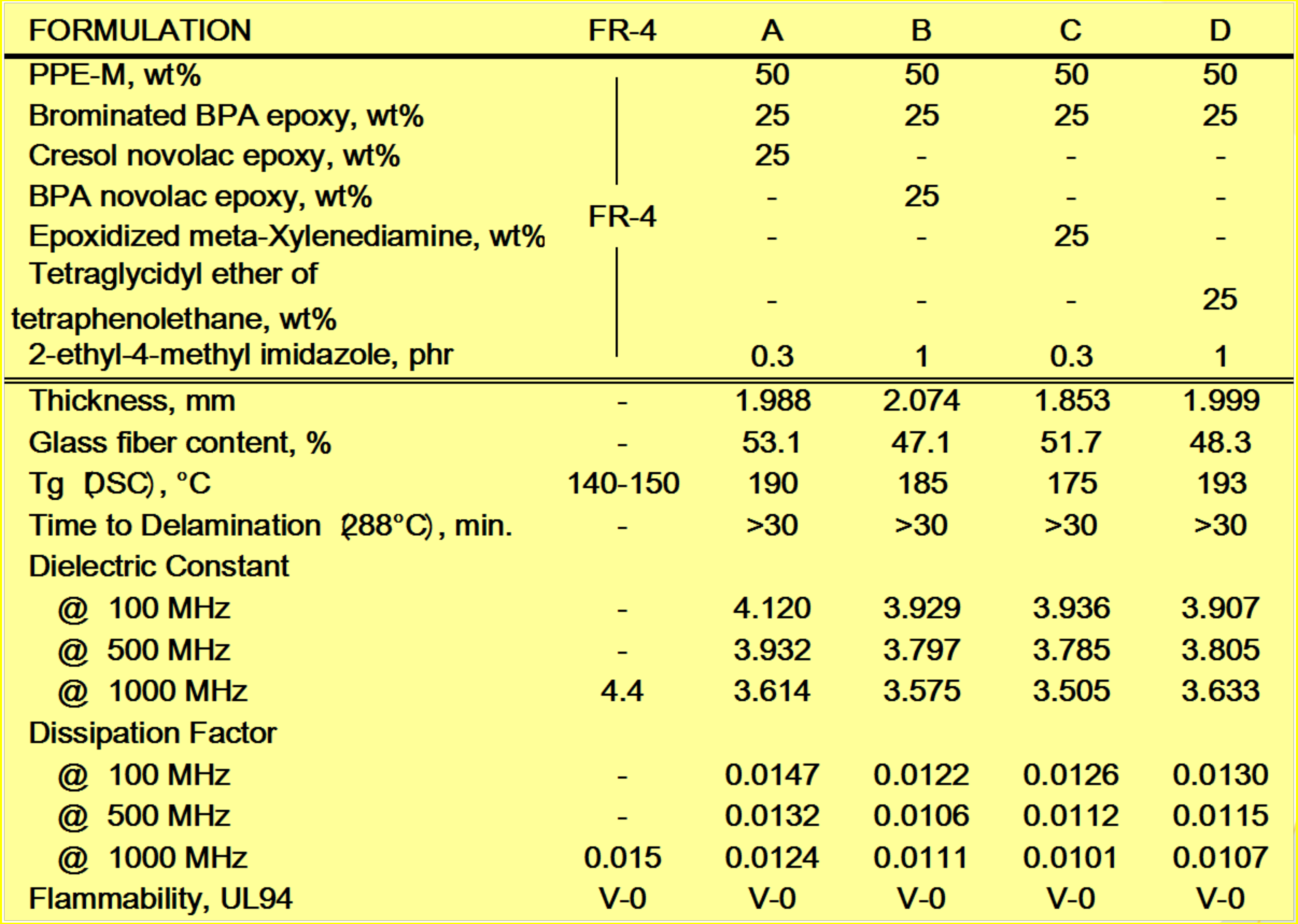






Laminates prepared for evaluation

EPOXY LAMINATES CONTAINING PPE-M



FORMULATION	FR-4	A	B	C	D
PPE-M, wt%	FR-4	50	50	50	50
Brominated BPA epoxy, wt%		25	25	25	25
Cresol novolac epoxy, wt%		25	-	-	-
BPA novolac epoxy, wt%		-	25	-	-
Epoxidized meta-Xylenediamine, wt%		-	-	25	-
Tetraglycidyl ether of tetraphenolethane, wt%		-	-	-	25
2-ethyl-4-methyl imidazole, phr		0.3	1	0.3	1
Thickness, mm	-	1.988	2.074	1.853	1.999
Glass fiber content, %	-	53.1	47.1	51.7	48.3
Tg (DSC), °C	140-150	190	185	175	193
Time to Delamination (288°C), min.	-	>30	>30	>30	>30
Dielectric Constant					
@ 100 MHz	-	4.120	3.929	3.936	3.907
@ 500 MHz	-	3.932	3.797	3.785	3.805
@ 1000 MHz	4.4	3.614	3.575	3.505	3.633
Dissipation Factor					
@ 100 MHz	-	0.0147	0.0122	0.0126	0.0130
@ 500 MHz	-	0.0132	0.0106	0.0112	0.0115
@ 1000 MHz	0.015	0.0124	0.0111	0.0101	0.0107
Flammability, UL94	V-0	V-0	V-0	V-0	V-0

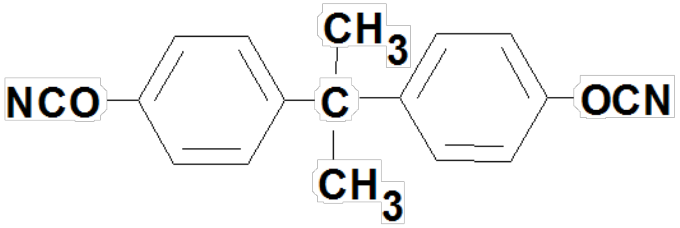
High Tg, low Dk, Df Laminates

SUMMARY: PPE-M in EPOXY RESINS

PPE-M in epoxy resins:

- **PPE-M reacts with epoxy resins**
- **Stable, single phase morphology**
- **Decrease in dielectric properties**
- **Increase in T_g**
- **Increase in toughness**
- **Lower moisture uptake**
- **More stable dielectric properties on exposure to moisture**
- **High T_g laminates with low dielectric properties**

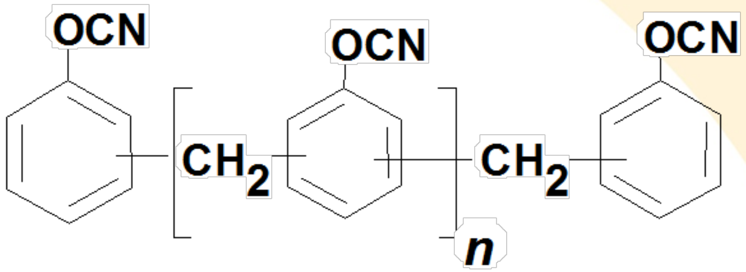
EVALUATION in CYANATE ESTERS (CE)



BPA-CE

Bisphenol A cyanate ester

Lonza – Primaset® BADCy



PN-CE

Phenol novolac cyanate ester

Lonza - Primaset® PT-30

Evaluation of PPE-M in castings

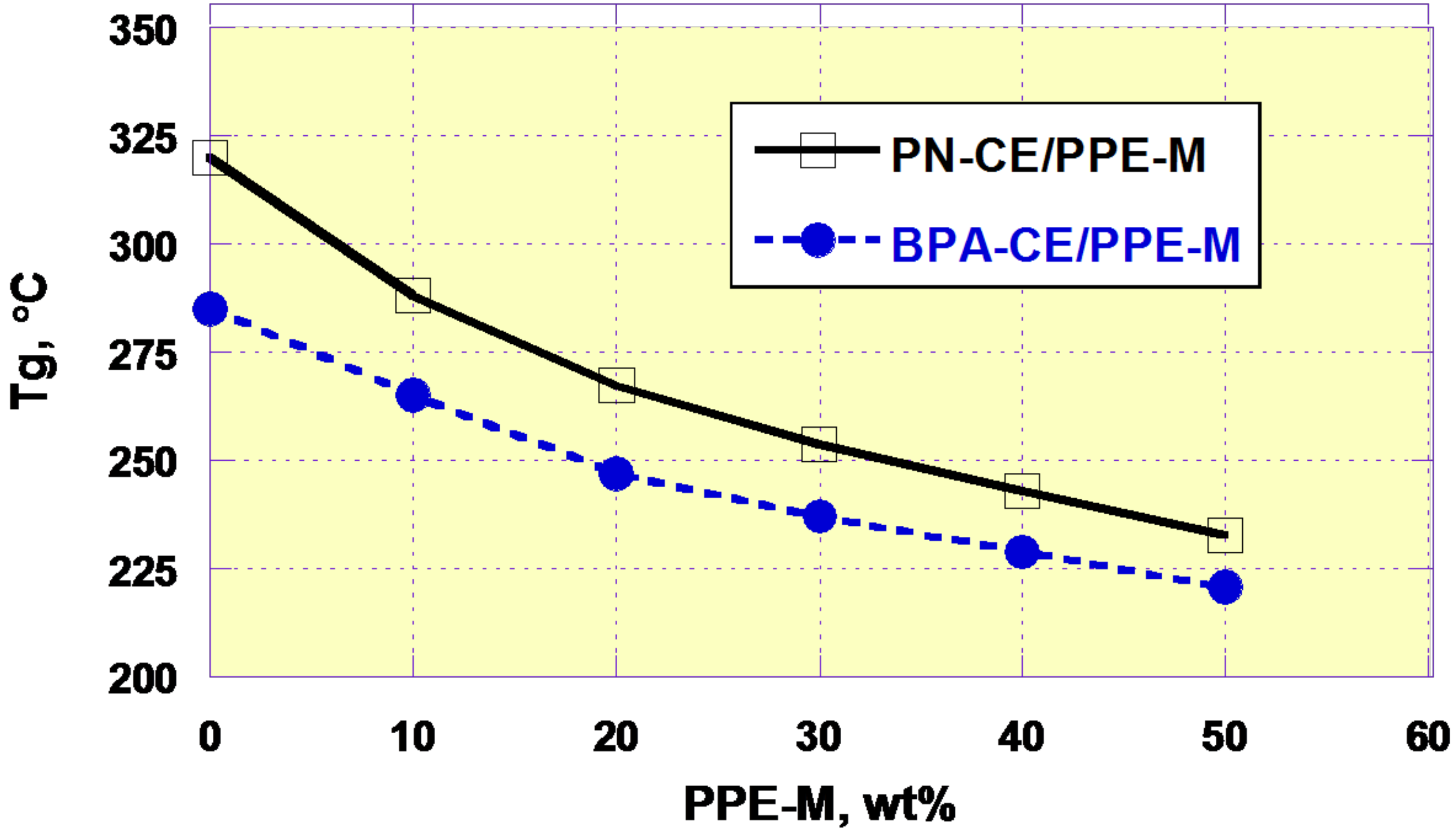
- **Resin only - no glass fiber or filler**
- **Unfettered by confounding factors from fillers or reinforcement materials**

BPA-CE/PPE-M and PN-CE/PPE-M sample designations

Primaset® is trademark of Lonza Group Ltd.

EFFECT of PPE-M on T_g of CYANATE ESTERS

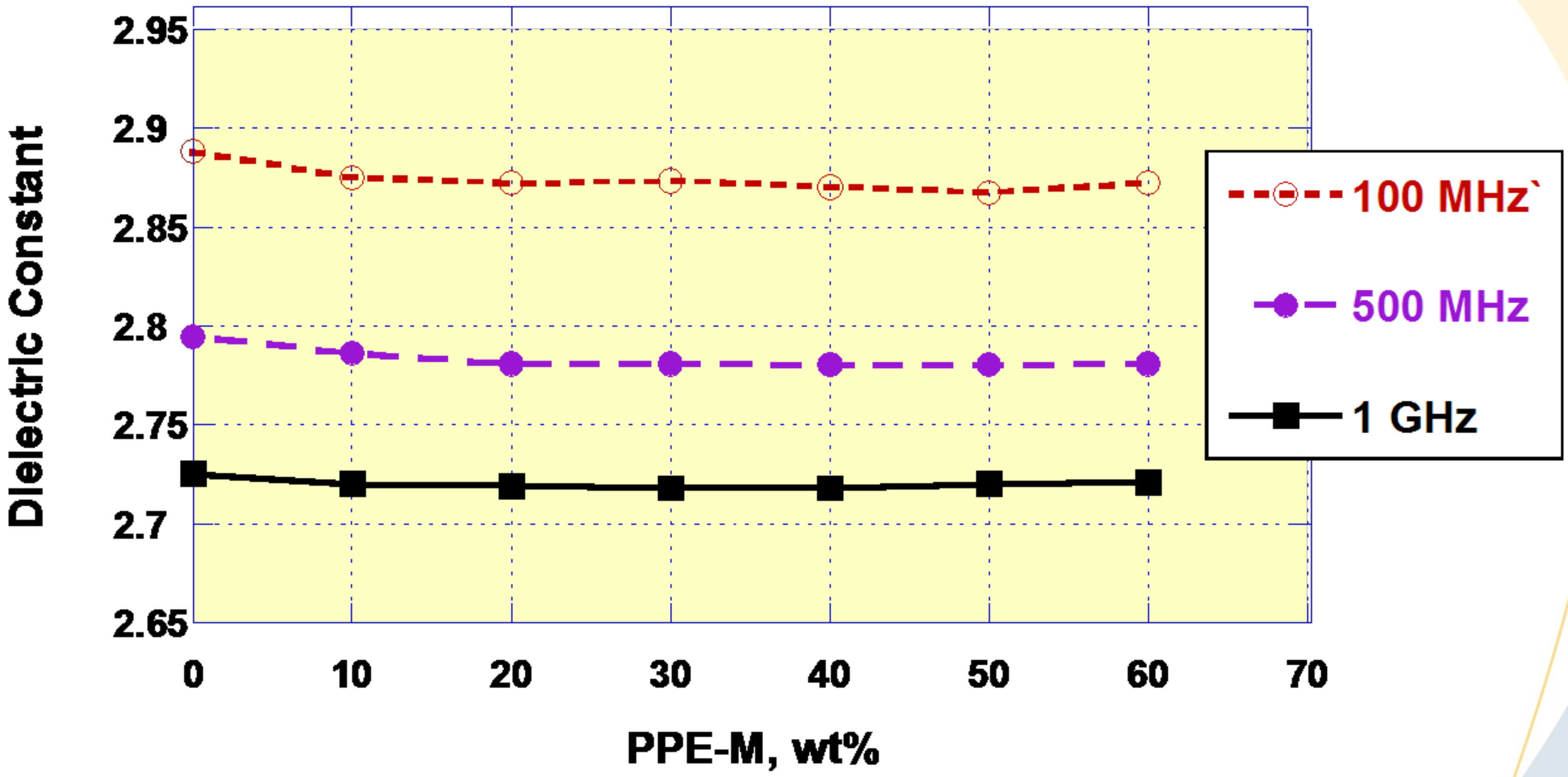
Determined by DSC @ 20°C/min



- T_g decreases with PPE-M levels
- T_g >220°C at 50% PPE-M

EFFECT of PPE-M on D_k of CYANATE ESTERS

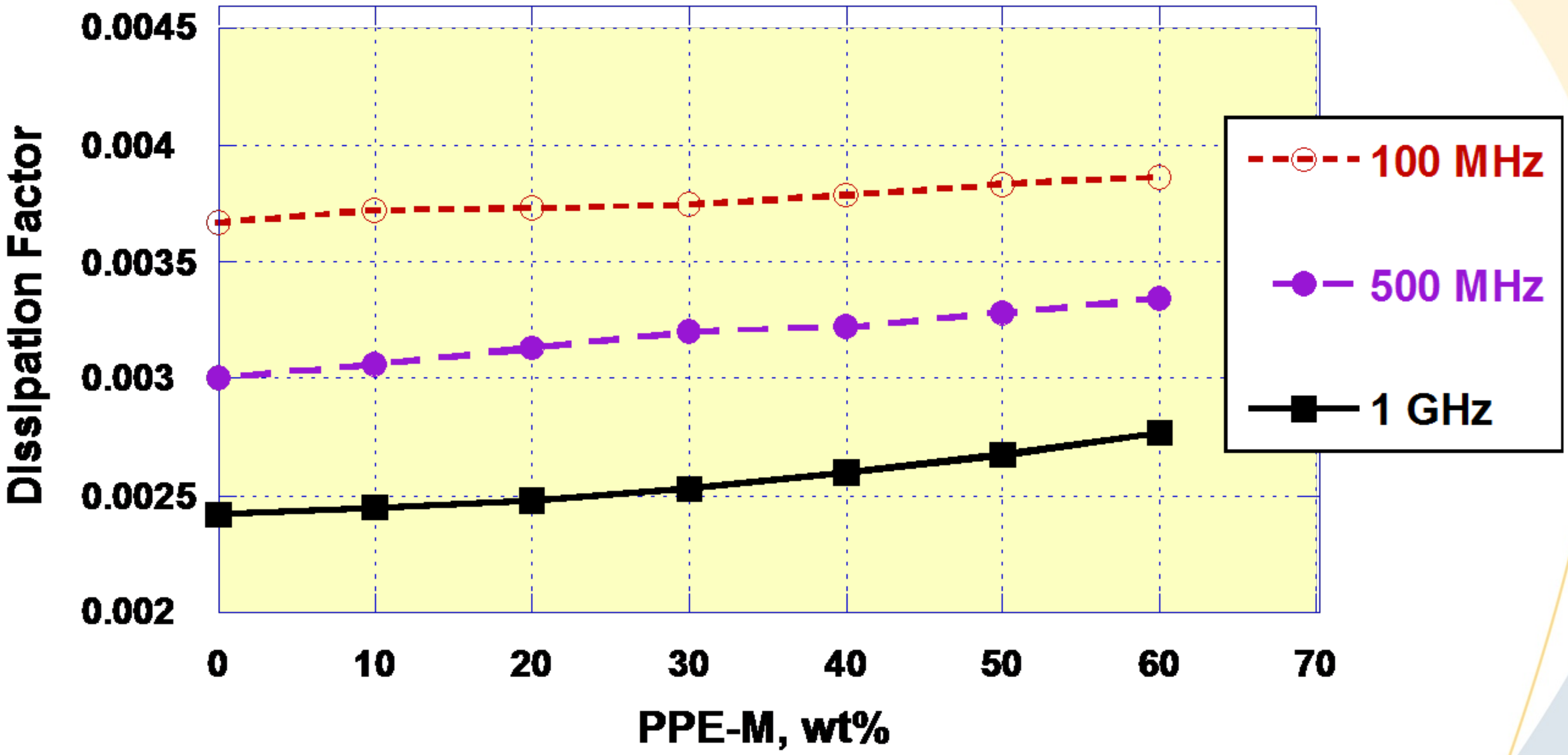
Measured using parallel plate technique



D_k - low with little change versus PPE-M level

EFFECT of PPE-M on D_f of CYANATE ESTERS

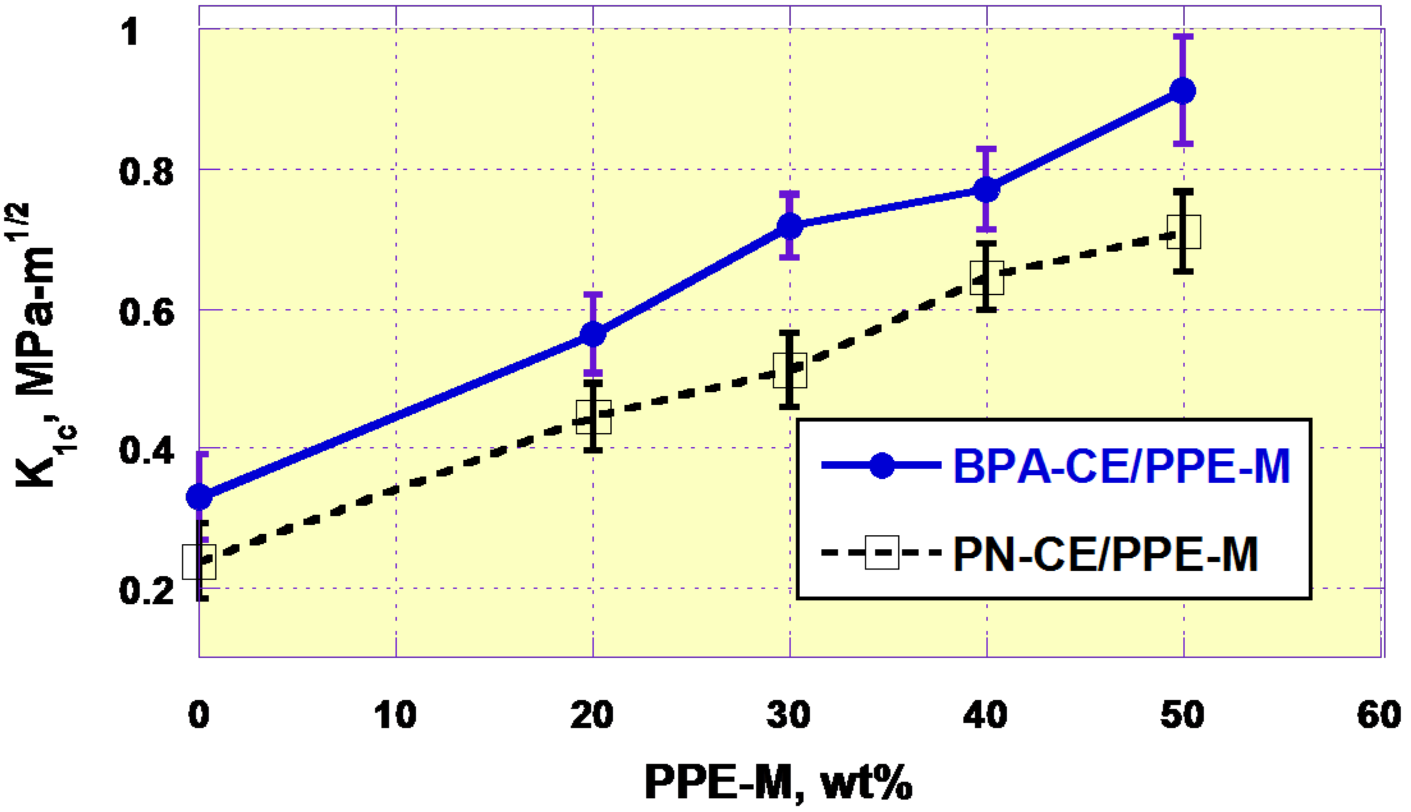
Measured using parallel plate technique



D_f - low with slight increase versus PPE-M level

EFFECT of PPE-M on FRACTURE TOUGHNESS

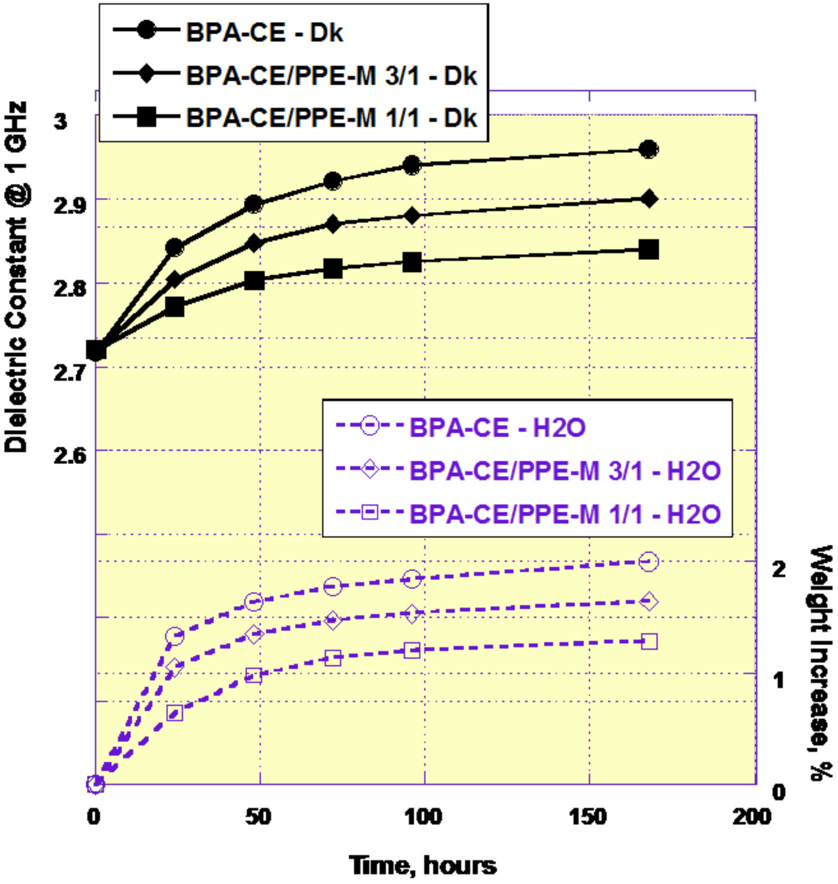
of CYANATE ESTER RESINS

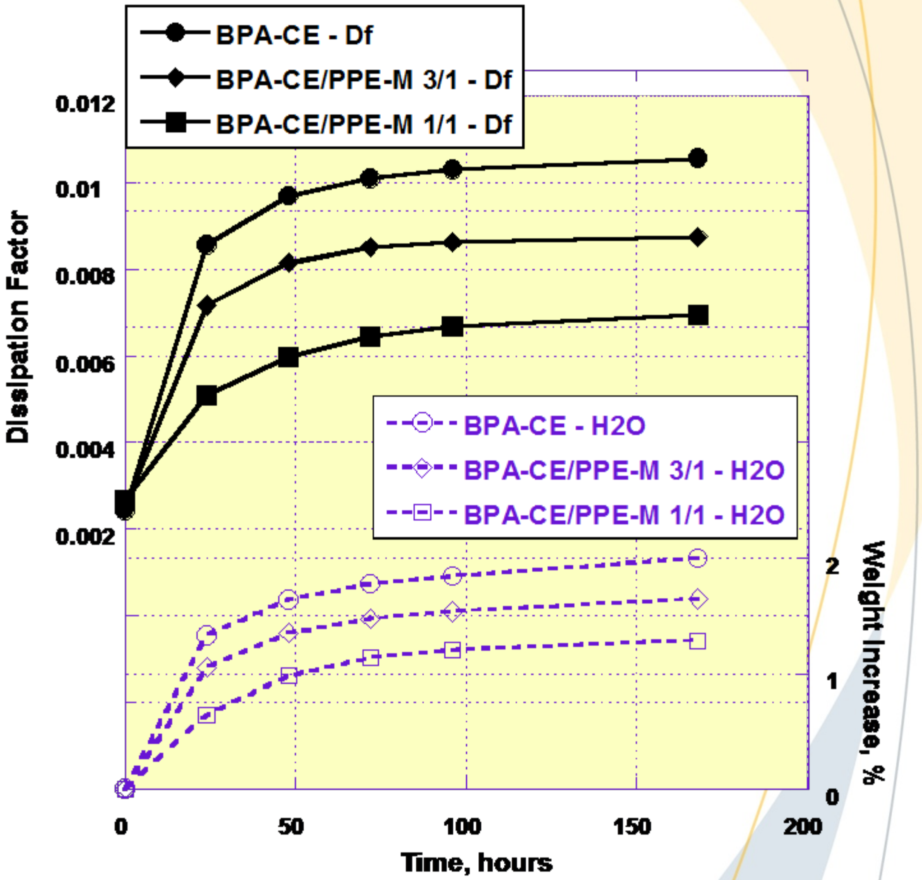


Toughness increases with PPE-M level

EFFECT of PPE-M on H_2O UPTAKE and DIELECTRIC PROPERTIES of BPA-CE

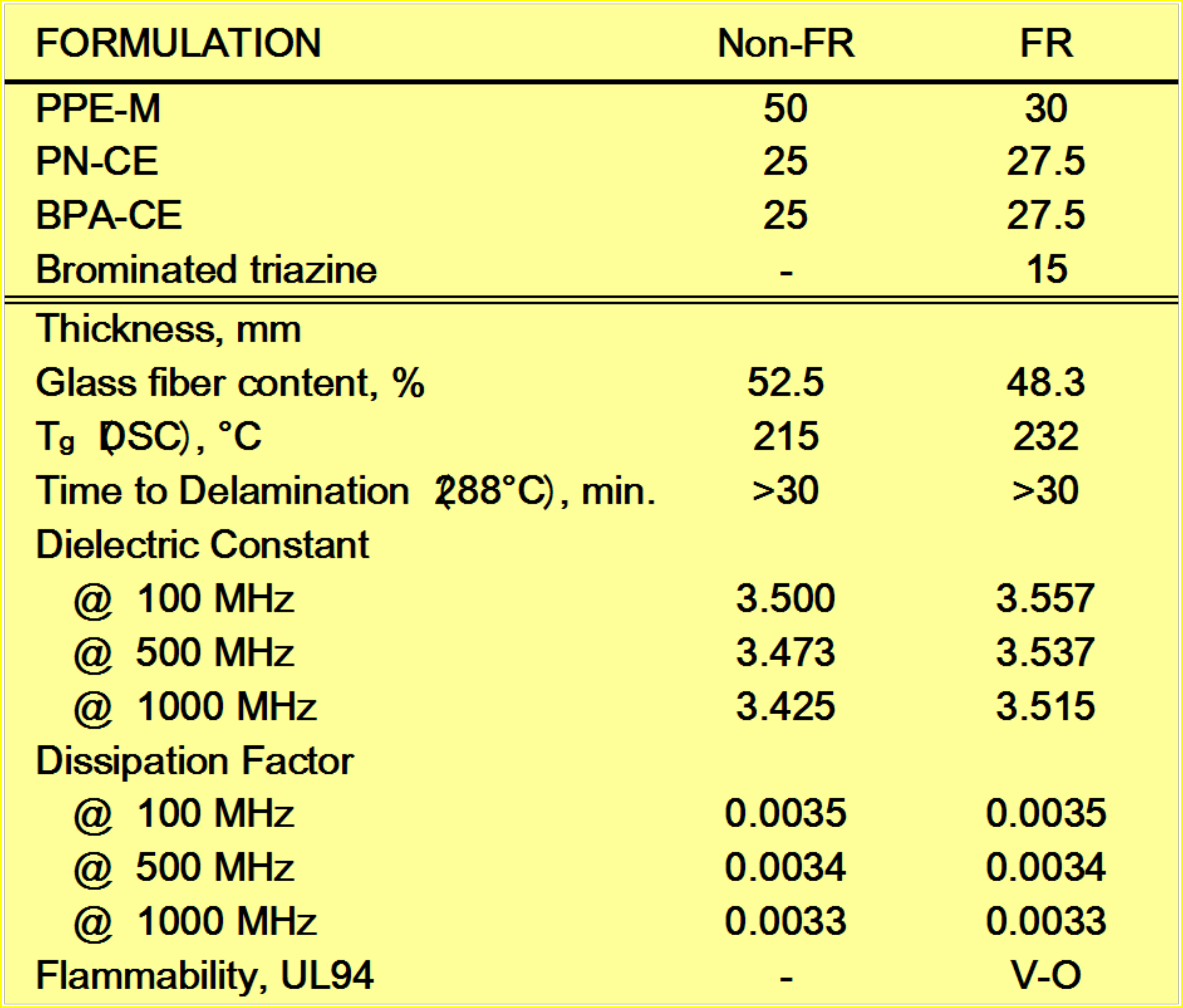
Effect of Moisture: Samples conditioned by immersion in water at 80°C





- ➢ PPE-M decreases H_2O uptake
- ➢ PPE-M gives less change in dielectric properties

CYANATE ESTER LAMINATES CONTAINING PPE-M



FORMULATION	Non-FR	FR
PPE-M	50	30
PN-CE	25	27.5
BPA-CE	25	27.5
Brominated triazine	-	15
Thickness, mm		
Glass fiber content, %	52.5	48.3
T_g (DSC), °C	215	232
Time to Delamination (288°C), min.	>30	>30
Dielectric Constant		
@ 100 MHz	3.500	3.557
@ 500 MHz	3.473	3.537
@ 1000 MHz	3.425	3.515
Dissipation Factor		
@ 100 MHz	0.0035	0.0035
@ 500 MHz	0.0034	0.0034
@ 1000 MHz	0.0033	0.0033
Flammability, UL94	-	V-O

Brominated triazine =
tris(2,4,6-tribromophenoxy)-1,3,5-triazine

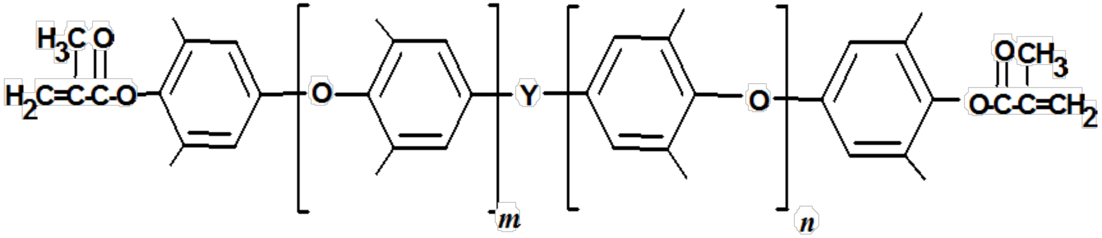
High T_g, low D_k, D_f Laminates

SUMMARY: PPE-M in CYANATE ESTER RESINS

PPE-M in cyanate ester resins:

- **PPE-M reacts with cyanate esters**
- **Stable, single phase morphology**
- **Low dielectric properties, little change**
- **Decrease in T_g (>220°C at 50 wt%)**
- **Increase in toughness**
- **Lower moisture uptake**
- **More stable dielectric properties on exposure to moisture**
- **High T_g laminates with low dielectric properties**

METHACRYLATE ESTER of PPE-M



For use in non-epoxy and non-cyanate ester resins

Reaction with unsaturated monomers such as:

- **TAIC (triallyl isocyanurate)**
- **Styrenic monomers**
  - **t-butyl styrene (TBS)**
  - **divinylbenzene (DVB)**
  - dibromostyrene (DBS)
- Di- and poly- (meth)acrylates
- Vinyl-terminated polytbutadiene

Castings prepared for evaluation

EVALUATION in CASTINGS

Resin only - no glass fiber or filler

Castings cured with 1.5 phr 2,5-dimethyl-2,5-di(t-butylperoxy)hexane

FORMULATION	E	F
Methacrylated PPE-M	50	50
TBS	40	-
DVB	10	-
TAIC	-	50
T_g (DSC), °C	194	198
Dielectric Constant		
@ 1 GHz	2.55	2.75
@ 2.4 GHz	2.53	2.73
@ 10 GHz	2.52	2.71
Dissipation Factor		
@ 1 GHz	0.0038	0.0049
@ 2.4 GHz	0.0037	0.0048
@ 10 GHz	0.0036	0.0046

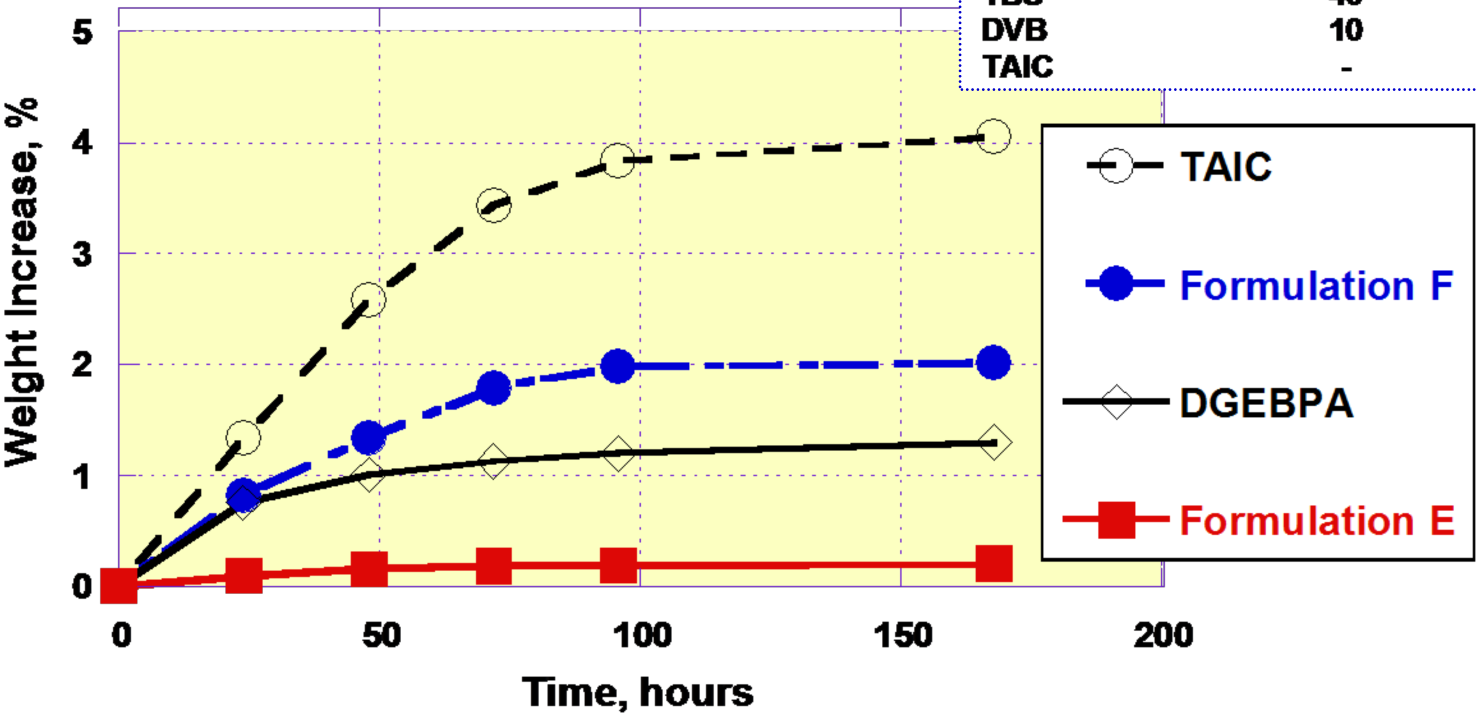
Dielectric properties measured using resonant cavity technique

High T_g, low D_k, D_f castings

EFFECT of Methacrylated PPE-M on H_2O UPTAKE

Moisture uptake:
Sample immersion in water at 80°C

FORMULATION	E	F
Methacrylated PPE-M	50	50
TBS	40	-
DVB	10	-
TAIC	-	50



- ➢ In TAIC, H_2O uptake decreased with PPE-M
- ➢ PPE-M/TBS/DVB (E) has very low H_2O uptake

SUMMARY: Methacrylated PPE-M in VINYL RESINS

Methacrylated PPE-M in vinyl resins:

- **Methacrylated PPE-M reacts with vinyl resins**
- **Stable, single phase morphology**
- **Low dielectric properties**
- **High T_g**
- **Lower moisture uptake**

SUMMARY

POLYPHENYLENE ETHER MACROMONOMERS

- **Reacts with various thermoset resins**
  - **Epoxy, cyanate esters, vinyl resins**
- **Gives stable, single-phase morphology**
- **Enhances properties of dielectric materials**
  - **T_g – higher in epoxy resins**

    - lower in cyanate esters, but >220°C
  - **Dielectric properties - lower in epoxy resins**

    - similar in cyanate esters
  - **Increased toughness**
  - **Lower H_2O uptake**
  - **More stable dielectric properties on exposure to moisture**

Thank you