Bifunctional Low Molecular Weight Polyphenylene Ether Resins for PWB Base Materials

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Abstract

A new bifunctional low molecular weight polyphenylene ether (OPE oligophenylene ether) was obtained by the oxidative coupling of 2,2',3,3',5,5'-hexamethyl-[1,1'-biphenyl]-4,4'-diol (HMBP hexamethylbiphenol) and 2,6-dimethylphenol, and several thermosetting resins were synthesized from OPE by changing the end hydroxyl group into other reactive functional groups such as glycidyl ether group(OPE-2Gly) and vinylbenzyl ether group(OPE-2ST). These thermosetting resins keep such superior characteristics of high molecular weight polyphenylene ether(PPE) as low dielectric constant(Dk), low dielectric dissipation factor(Df), high glass transition temperature(Tg) and low water absorption rate, while formability in press and low solubility in organic solvents are desirably to be improved. A cured product of OPE-2ST had Tg :220˚C(DMA), Dk(10GHz):2.46, Df(10GHz):0.0020. A curable resin composition containing OPE-2ST and thermoplastic elastomer such as styrene-butadiene-styrene copolymer (SBS) and hydrogenated styrene-butadiene-styrene copolymer (SEBS) was able to form a curable film by solution casting method. Cured film obtained with aforementioned curable one containing OPE-2ST and SEBS kept high Tg of OPE-2ST because of micro phase separation. Characteristics of the film were Tg:200˚C (TMA), Dk (10GHz) :2.29, Df(10GHz) :0.0011. The Df value of this film was close to that of polytetrafluoroethylene (PTFE). These resins are accordingly suitable for printed wiring board (PWB) base materials in high-speed communication or telecommunication applications.

Introduction

As functions of electronic equipment become more sophisticated, higher performance and higher reliability are required for PWB. For example, in the field of large-volume and high-speed data transmission, PWB with lower transmission loss is needed to transmit more signals at a higher frequency. To reduce transmission loss, low dielectric constant and low dissipation factor are demanded for PWB base materials. Properties such as high heat resistance and low water absorption rate are also preferable for high reliability of electronic equipment.

PPE has high Tg and low dielectric properties, and has already been used as a resin for specialty laminate[*1]. However, producing PWB or laminate containing PPE is not always easy because of its low solubility in organic solvent and high melt viscosity because of its high molecular weight over 10000.

In this paper, OPE and OPE resins were developed as PWB base materials. These resins are thermosetting and such weak points of PPE as low solubility and high melt viscosity are overcome in these resins.

Experimental

Preparation of OPE and OPE derivatives

OPE was synthesized by the oxidative coupling of HMBP and 2,6-dimethylphenol with copper/amine catalyst. OPE-2Gly was synthesized from OPE by reacting it with epichlorohydrin in an alkaline condition. OPE-2ST was synthesized from OPE by reacting it with chloromethylstyrene in an alkaline condition.

Preparation of cured resin

Cured resin of OPE-2Gly was prepared by casting the resin solution, which contained OPE-2Gly and phenol novolac (PN) as a hardener, onto polyimide film, evaporating the solvent to make brittle resin film, rubbing it into resin powder, and then pressing the powder into 1.0mm-thick specimen using a SUS spacer. The pressing was carried out for 1 hour at 180˚C under vacuum and the curing was afterwards continued for 9 hours at 180˚C. Cured resin of OPE-2ST was prepared by pressing the powder of OPE-2ST without any hardener into 1.0mm-thick specimen using a SUS spacer for 1hour at 200˚C under vacuum, followed by the curing for 2 hours at 200˚C.

Preparation of cured film

Cured film containing OPE-2ST and thermoplastic elastomer was prepared by dissolving them into the solvent, casting the resin solution onto ethylene-tetrafluoroethylene copolymer(ETFE) film, evaporating the solvent to make film, curing it for 1 hour at 200˚C under nitrogen, and peeling it off from the ETFE film. SBS and SEBS were used as thermoplastic elastomer. Content of polystyrene was 43wt% in SBS and 29wt% in SEBS. Weight average molecular weight was 1.1×10^5 for SBS and 9.3×10^4 for SEBS.

Preparation of laminate

Copper clad laminate was made by impregnating the resin solution containing OPE-2ST and SEBS into glass fabric, evaporating solvent to get prepregs, and pressing them with copper foils for 1 hour at 200˚C under vacuum.

Properties of OPE and OPE derivatives

Number average molecular weight (Mn) and weight average molecular weight(Mw) were determined by gel permeation chromatography(GPC) with polystyrene standard. Hydroxyl equivalent weight of OPE and epoxy equivalent weight of OPE-2Gly were measured by titrimetric method. Vinylbenzyl ether equivalent weight of OPE-2ST and hydroxyl equivalent weight of PPE were measured by infrared spectroscopy. Solubility was observed at concentration of 50wt%. Toluene and methylethylketone (MEK) were used as solvent. Complex viscosity was measured by rheometer at temperature increasing rate of 5˚C/min.

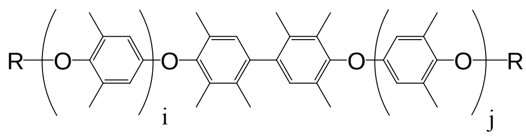
Properties of cured resin, cured film and laminate

Tg was measured by dynamic mechanical analysis (DMA) and thermal mechanical analysis(TMA). Dielectric properties were measured by perturbation method using cavity resonator at 25˚C. Micro phase separation of film was observed by scanning transmission electron microscope (STEM). Transmission loss of laminate up to 20GHz was measured by network analyzer (line length: 300mm, dielectric thickness:0.1mm, copper foil:18μm, characteristic impedance:50Ω, temperature:25˚C).

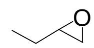
Result and Discussion

OPE and OPE derivatives

Figure1 shows molecular structures of OPE and OPE derivatives. Structures were determined by nuclear magnetic resonance (NMR) analysis. OPE is provided with PPE structure on both sides of the HMBP core.



OPE : R = H

OPE-2Gly : R = 

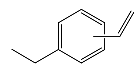
OPE-2ST : R = 

Figure1 - Molecular structure of OPE and OPE derivatives

General properties of OPE and OPE derivatives are shown in Table1. Molecular weight of OPE was controlled by mole ratio of 2,6-dimethylphenol and HMBP in polymerization. Two kinds of OPE with different molecular weight were prepared. OPE-2Gly was synthesized from OPE (1). OPE-2ST (1) was synthesized from OPE-(1), and OPE-2ST(2) was synthesized from OPE(2).

Table1 - Properties of OPE and OPE derivatives

Sample name	OPE(1)	OPE(2)	OPE-2Gly	OPE-2ST(1)	OPE-2ST(2)	PPE
Mn	9.3×10^2	2.0×10^3	9.7×10^2	1.2×10^3	2.3×10^3	1.7×10^4
Mw	1.5×10^3	3.5×10^3	1.6×10^3	1.7×10^3	3.8×10^3	3.5×10^4
End group equivalent weight (g/eq)	4.7×10^2	9.9×10^2	5.0×10^2	5.8×10^2	1.2×10^3	1.3×10^4
Solubility in toluene (50wt%)	soluble	soluble	soluble	soluble	soluble	partially soluble
Solubility in MEK (50wt%)	soluble	partially insoluble	soluble	soluble	partially insoluble	insoluble

The end group equivalent weight of OPE and OPE derivatives was about half of their respective Mn. On the other hand, the hydroxyl equivalent weight of PPE was close to its Mn. These indicate that OPE and OPE derivatives are bifunctional. OPE and OPE derivatives dissolved into toluene or MEK at higher concentration in comparison with PPE. In toluene, OPE and OPE derivatives dissolved over 50wt%. In MEK, solubility tends to be lower, as molecular weight of OPE becomes higher.

Figure2 shows that softening point of OPE is lower than that of PPE. This is because molecular weight of OPE is lower than that of PPE. As a result of lowering the softening point, melt viscosity of OPE is lower than that of PPE.

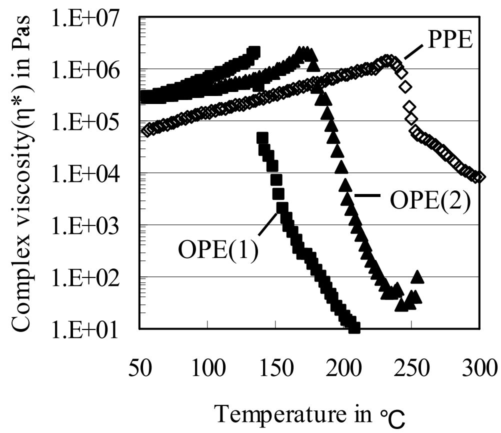


Figure2 - Profile of rheometer

Cured resin of OPE derivatives

Table2 shows properties of cured resins. The cured resin of OPE-2Gly/PN had lower Dk, lower Df, lower water absorption rate than the cured resin of phenol novolac epoxy (PNepoxy)/PN. It is known that a polar end group such as hydroxyl group affects dielectric properties[*2] and water absorption rate. Therefore, in order to lower dielectric properties and water absorption rate, number of polar end group in the resin should be reduced. In OPE-2Gly, OPE structure plays a role of decreasing concentration of end hydroxyl group in cured resin. The cured resin of OPE-2ST was obtained by only heating without a hardener or an initiator. The cured resin of OPE-2ST (2) had almost the same Tg, dielectric properties and water absorption rate as PPE.

Table2 - Propeties of cured resins

Cured resin			OPE-2Gly /PN	OPE-2ST (1)	OPE-2ST (2)	PNepoxy /PN	PPE
Glass transition temperature (Tg)	DMA(10Hz)	˚C	167	252	226	160	226
	TMA	˚C	127	218	201	132	203
Dielectric constant (Dk)	1GHz	-	2.92	2.63	2.61	3.17	2.50
	10GHz	-	2.70	2.49	2.46	2.81	2.46
Dissipation factor (Df)	1GHz	-	0.0206	0.0030	0.0023	0.0314	0.0018
	10GHz	-	0.0249	0.0028	0.0020	0.0344	0.0022
Water absorption rate	PCT*-100hr	wt%	1.2	0.2	0.2	1.7	0.4

*) Pressure Cooker Test at 121˚C under the pressure of 0.2MPa

Cured film of OPE-2ST

It was investigated whether OPE-2ST is able to be employed on an insulation material for build-up PWB, a curable film and a cured film or not. In only OPE-2ST, crack occurred in the curable film after evaporating solvent by casting method. Crack was prevented by using thermoplastic elastomer such as SBS and SEBS, both of which are used as a modifier of PPE. And the cured film was obtained by heating the curable film.

The effect of PPE structure in OPE on the formation of film was observed in comparison with etherified HMBP with vinylbenzyl compound without PPE structure as a reference. The film containing OPE-2ST (2) was transparent, but the film containing aforementioned etherified HMBP became turbid after evaporating solvent because of macro phase separation. In the film containing OPE-2ST, micro phase separation occurred (Figure3, 4).

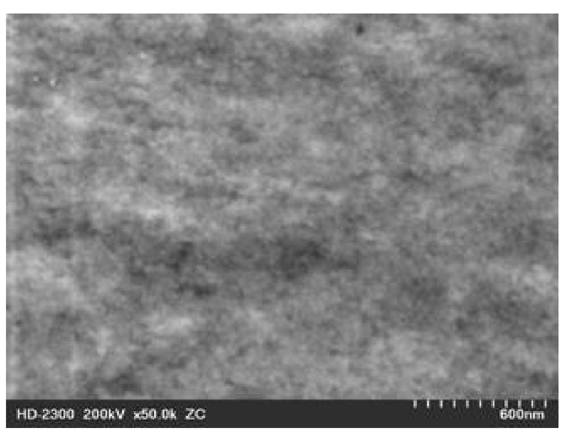


Figure3 - STEM image of film(OPE-2ST(2)/SBS)

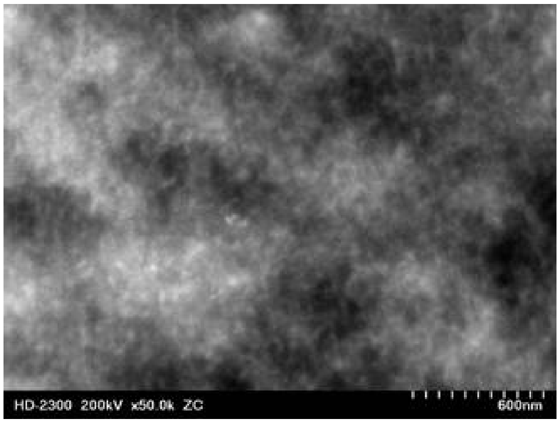


Figure4 - STEM image of film(OPE-2ST(2)/SEBS)

Figure5 shows that Tg became lower as content of thermoplastic elastomer increased. Tg of OPE-2ST (2)/SEBS was about 40˚K higher than that of OPE-2ST(2)/SBS at the same content of elastomer. In the film of OPE-2ST (2)/SBS, a part of polybutadiene reacts with vinyl group of OPE-2ST, and micro phase separation is partially broken. On the other hand, in the film of OPE-2ST/SEBS, SEBS doesn't react with OPE-2ST, and clear micro phase separation therefore occurs. The difference in micro phase separation results in the difference of Tg.

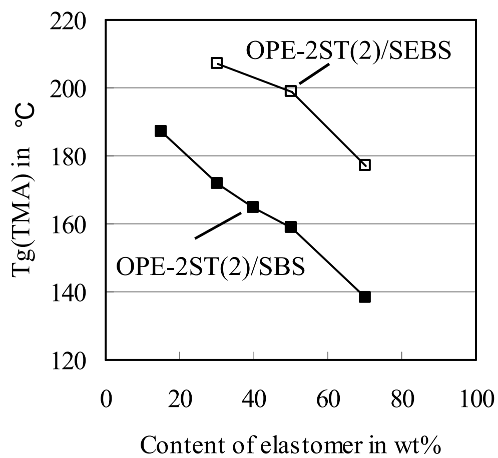


Figure5 - Glass transition temperature (Tg) of film

Figure6 shows that elastic modulus became lower as elastomer increased. Elastic modulus of OPE-2ST (2)/SEBS was lower than that of OPE-2ST(2)/SBS at the same content of elastomer. This is because the elastic modulus of SEBS used in this research is lower than that of SBS. Elastic modulus of the film proportionally changed to the variation of the content of polystyrene in SBS and SEBS.

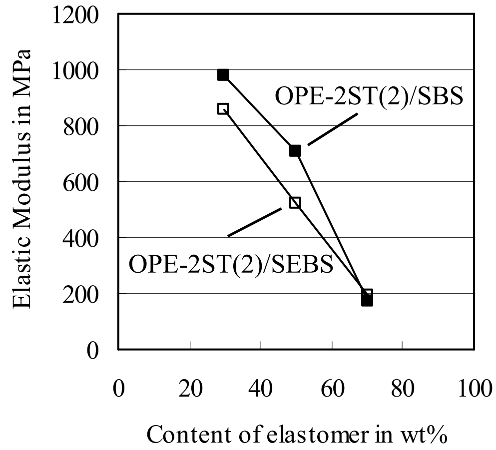


Figure6 - Elastic modulus of film

Figure7 and Figure8 show that Dk and Df of film are dependent on a kind and content of elastomer. By using SEBS which had lower dielectric properties than SBS and OPE-2ST (2), Dk and Df of the film respectively became less than 2.4 at 10GHz and less than 0.002 at 10GHz.

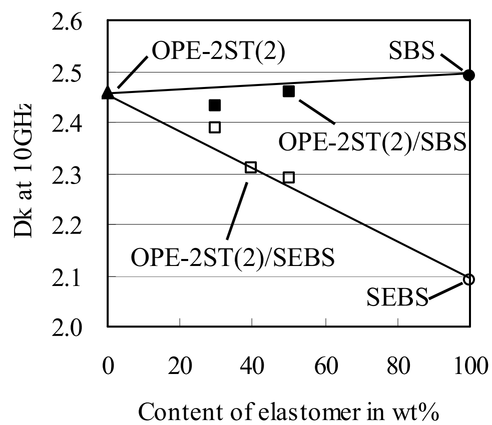


Figure7 - Dielectric constant (Dk) of film

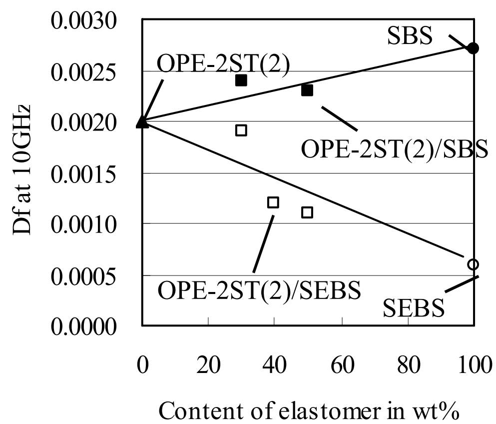


Figure8 - Dissipation factor (Df) of film

Laminate of OPE-2ST

Applicability of OPE-2ST to laminate was investigated by using resin composition containing OPE-2ST (2) and SEBS. Table3 shows properties of laminate. To obtain lower dielectric properties, low Dk glass fabric was used. The laminate using OPE-2ST/SEBS had nearly the same low transmission loss as PTFE/glass laminate (Figure9).

Table3 - Properties of laminates

Resin system			OPE-2ST(2)/SEBS	PTFE	Epoxy(FR-4)
Glass fabric			Low Dk	E	E
Dk	10GHz	-	2.95	2.45	3.90
Df	10GHz	-	0.0026	0.0034	0.0169
Copper foil peel strength	18µm-thick (low profile)	kN/m	1.1	-	1.3
Tg	TMA	˚C	188	<30	130
Flammability	UL-94	-	No flame resistance	V-0	V-0

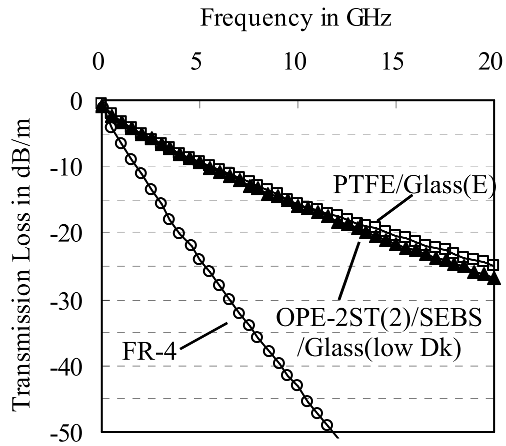


Figure9 - Transmission loss of laminate

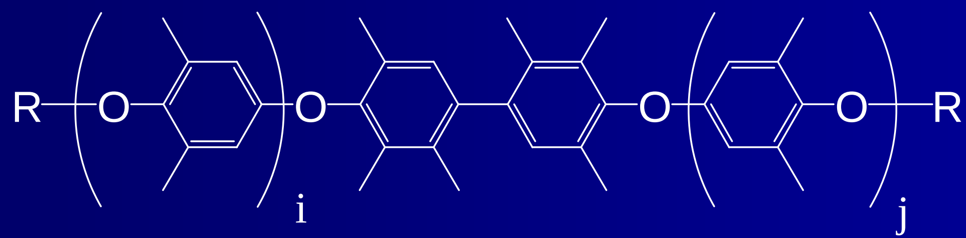
Summary

New thermosetting resins provided with low dielectric properties, low moisture absorption rate and high Tg were developed, and it was demonstrated that these resins can be used as base resins for PWB. In addition, they will be suitably employed on laminate, interlayer insulation film for build-up PWB, resin coated copper foil and so on.

References

1. H. S.-I. Chao et al, J. Appl. Polym. Sci., Vol.49, 1537-1546 (1993): K. Katayose et al: US patent 5,218,030
2. L. Hartshorn et al, Proc. Phys. Soc., Vol.52, 796-816 (1940)

Bifunctional low molecular weight polyphenylene ether (OPE) resins for PWB base materials



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Properties required for PWB base materials

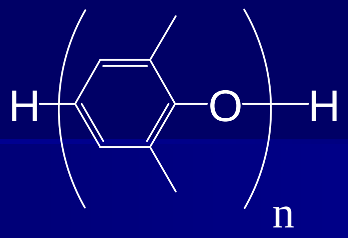
PWB

High-performance	Excellent reliability
Low transmission loss	Heat resistance (lead free reflow)
High stiffness	Through hole reliability (thermal cycle test)
High density interconnection	Copper ion migration resistance
.	High peel strength
.	.
.	.

Resin

Low dielectric constant (Dk)	High glass transition temperature (Tg)
Low dissipation factor (Df)	Low water absoption rate
High elastic modulus	Low coefficient of thermal expansion (CTE)
High insulation resistance	High adhesive property
.	.
.	.

Polyphenylene ether (PPE)



Conventionally used as a resin for high performance PWB

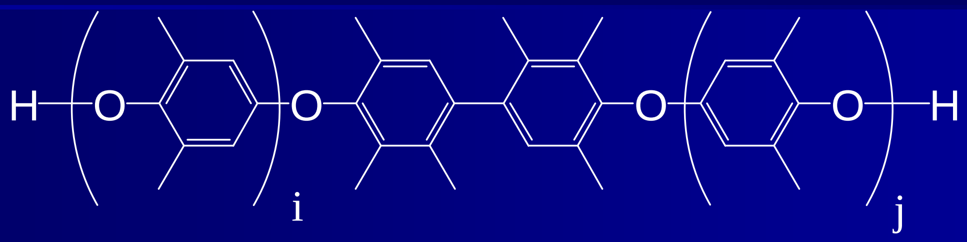
Properties

- ☺ Low Dk
- ☺ Low Df
- ☺ High Tg
- ☺ Low water absorption rate

- 😐 High molecular weight (>10,000)
- ☹ Low solubility in organic solvent
- ☹ High melt viscosity

What is OPE ?

Oligophenylene ether



PPE chemistry

- ☺ Low Dk
- ☺ Low Df
- ☺ High Tg
- ☺ Low water absorption rate

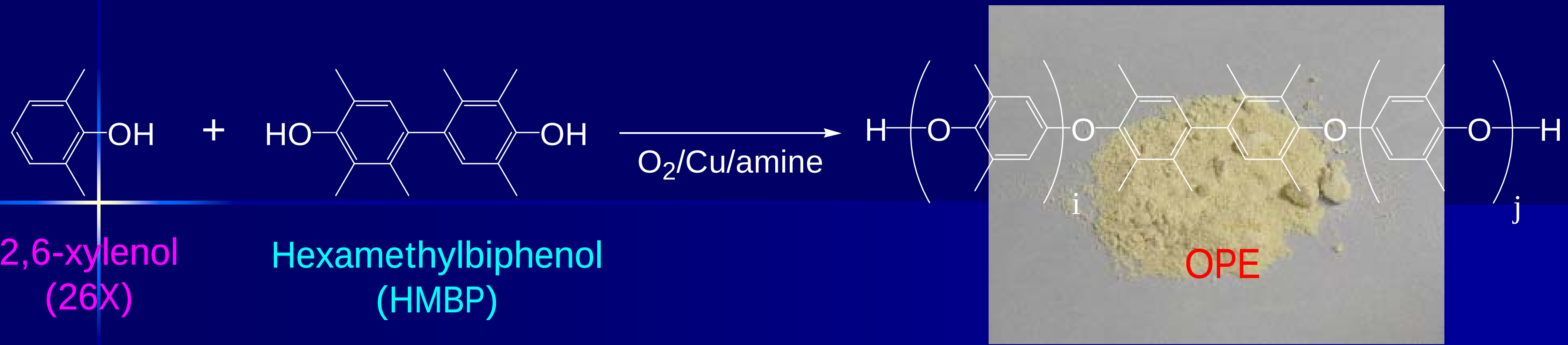
Oligomer

- ☺ High solubility in organic solvent
- ☺ Low melt viscosity

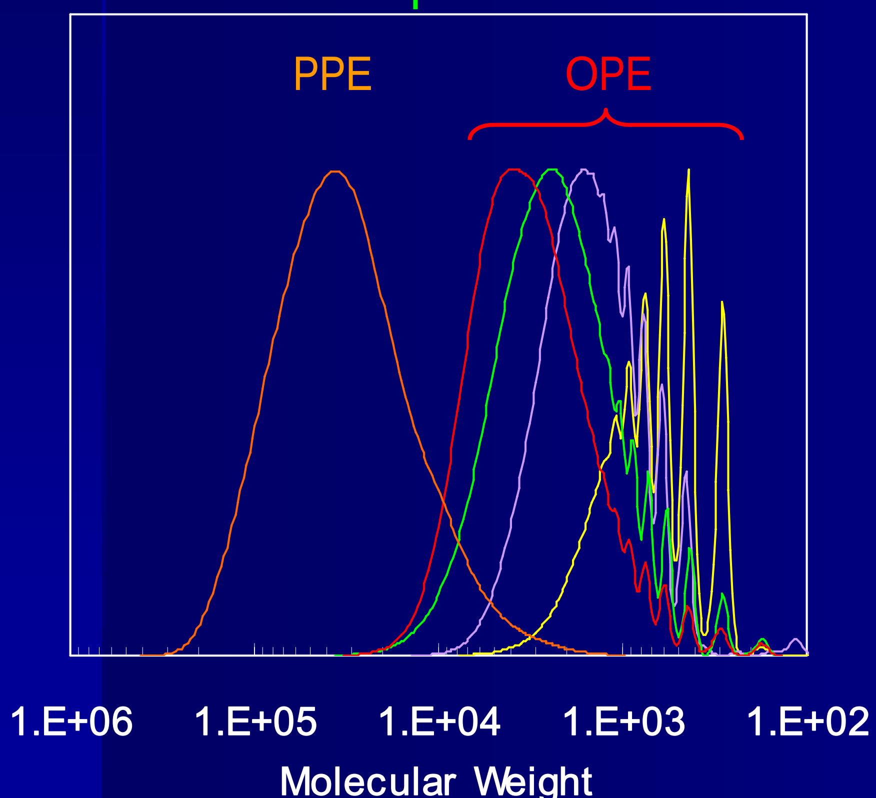
Bifunctional

- ☺ Curable

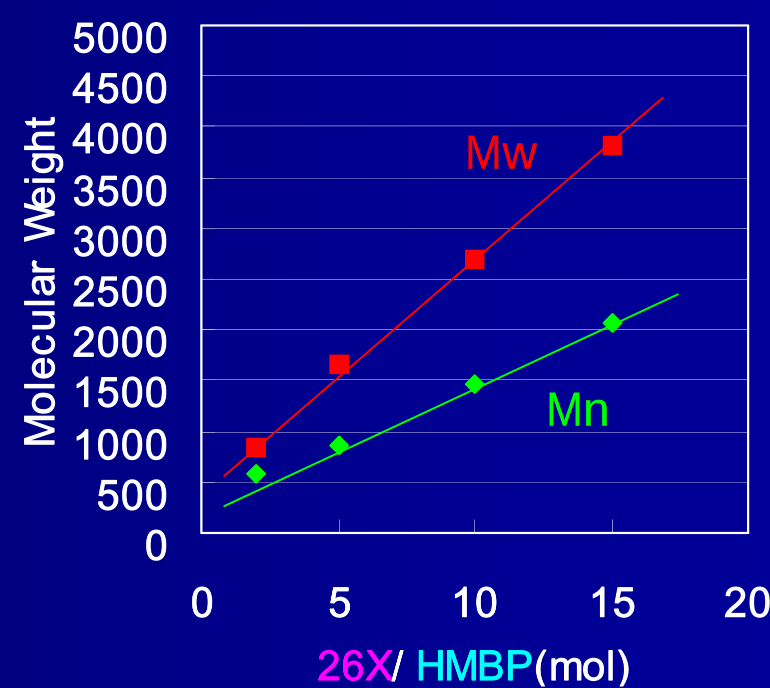
How to synthesize OPE ?



GPC profile

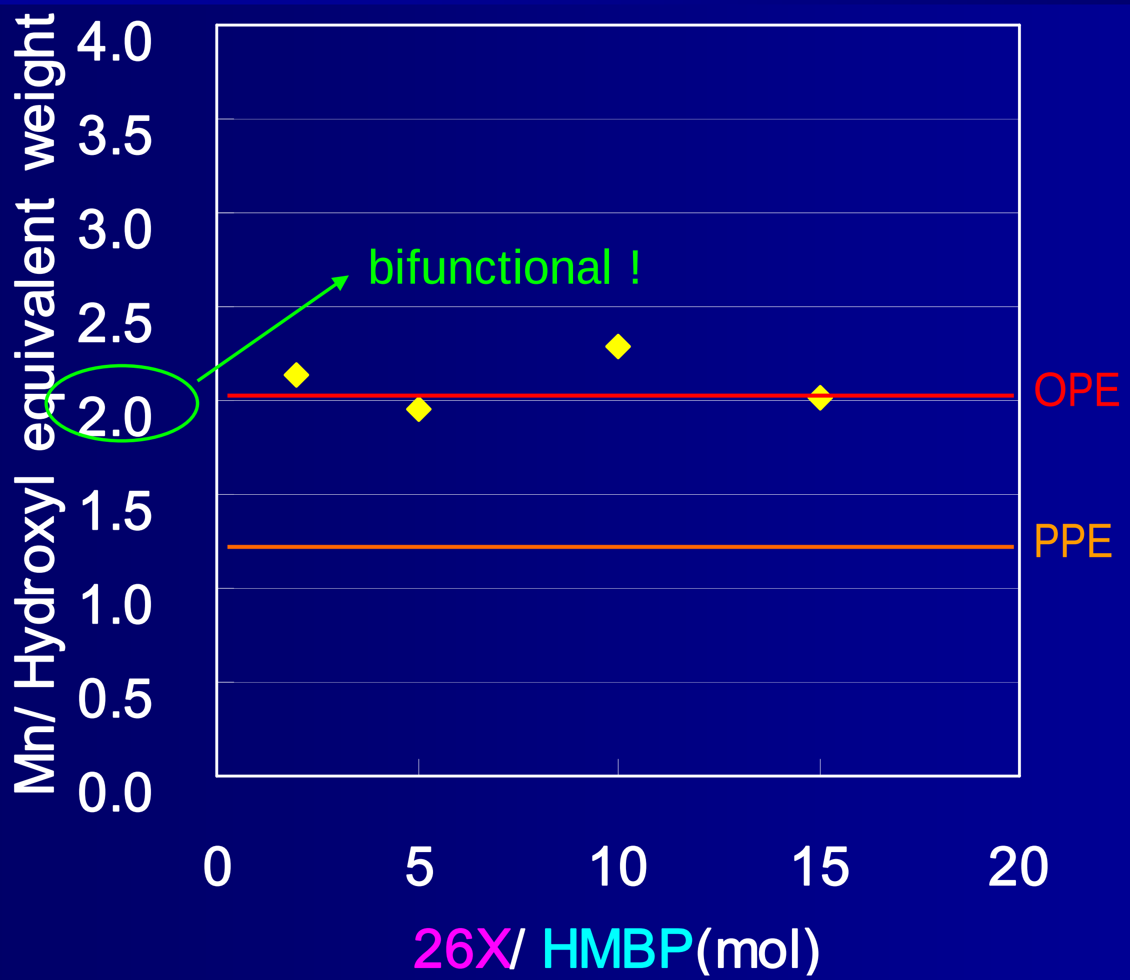


Molecular weight is fully controlled!

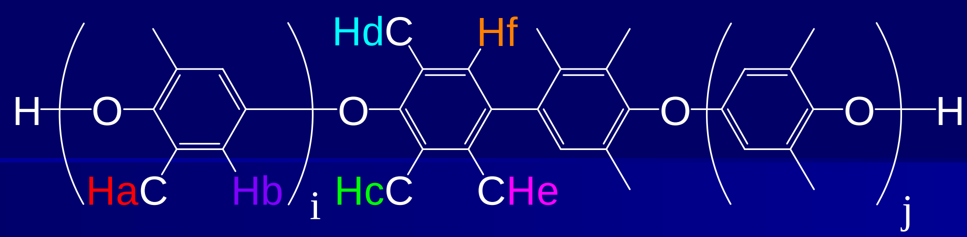


Mn : number average molecular weight
Mw : weight average molecular weight

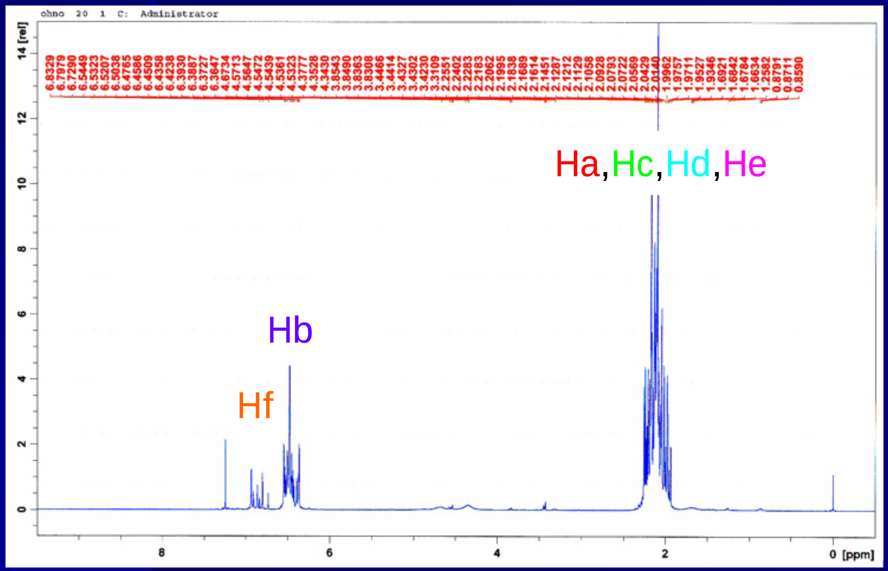
Number of end groups per molecule



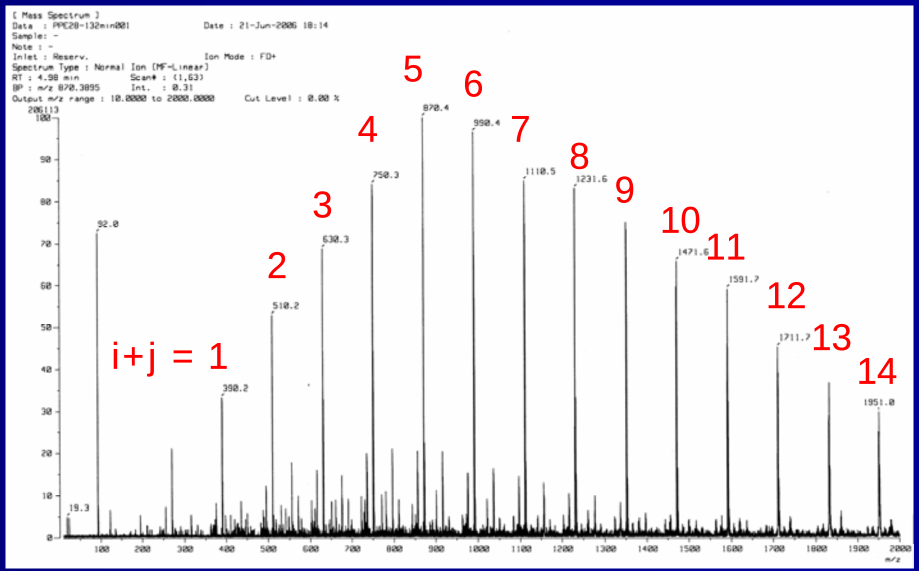
Identification of structure



^{1}H-NMR spectrum



MS spectrum



Solubility in organic solvent

Sample	Molecular weight		Solubility (50wt%)	
	Mn	Mw	Toluene	MEK
OPE(1)	930	1500	Soluble	Soluble
OPE(2)	2000	3500	Soluble	Partially insoluble
PPE	17000	35000	Partially soluble	Insoluble

Toluene

OPE(1) OPE(2) PPE

MEK(methylethylketone)

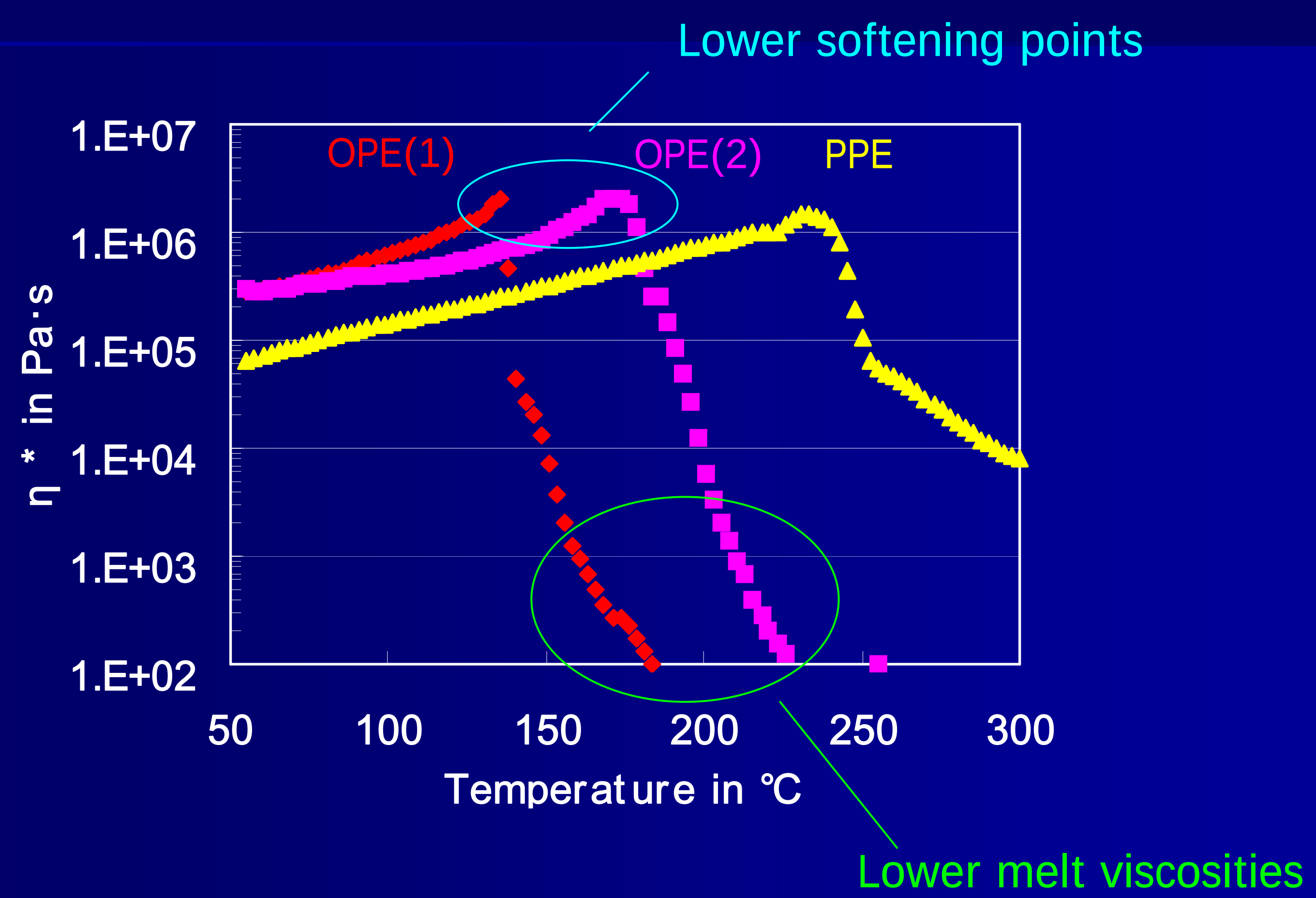
OPE(1) OPE(2) PPE

Sufficient solubility in organic solvents !

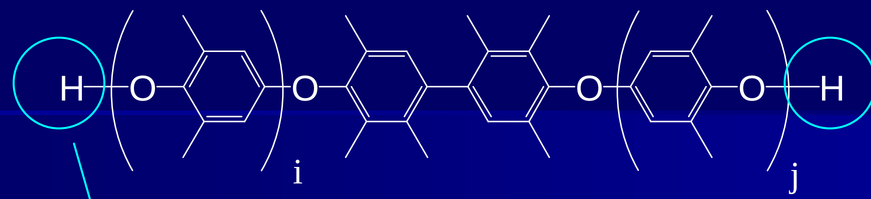
Profile of rheometer

(Viscosity as a function of temperature)

Test condition : ramp rate 5 ˚C /min, frequency 10rad/sec



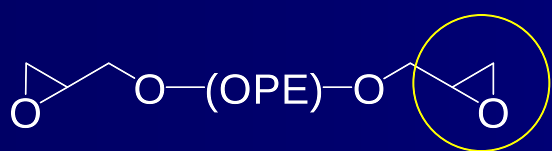
OPE derivatives



Convertible into reactive end groups

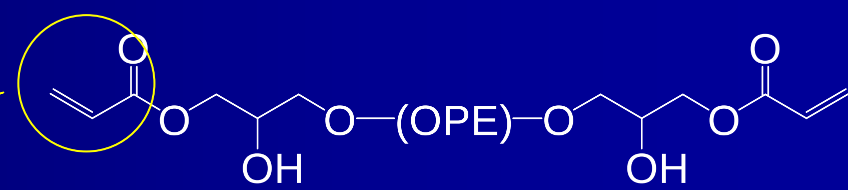
Thermosetting

Photocurable

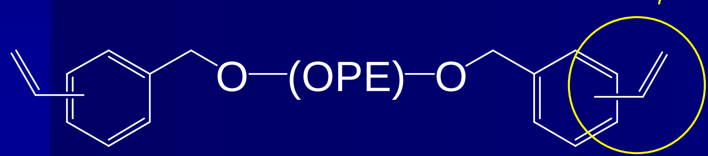


OPE-2Gly

Curable



OPE-2EA



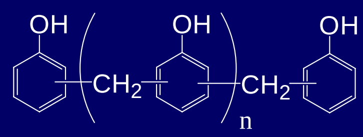
OPE-2ST

Solubility in organic solvent

Sample	Starting material	Molecular weight		Solubility (50wt%)	
		Mn	Mw	Toluene	MEK
OPE-2Gly(1)	OPE(1)	970	1600	Soluble	Soluble
OPE-2ST(1)	OPE(1)	1200	1700	Soluble	Soluble
OPE-2ST(2)	OPE(2)	2300	3800	Soluble	Partially insoluble
OPE-2EA(1)	OPE(1)	1300	2000	Soluble	Soluble

Sufficient solubility in organic solvents !

Processing conditions to obtain cured resins



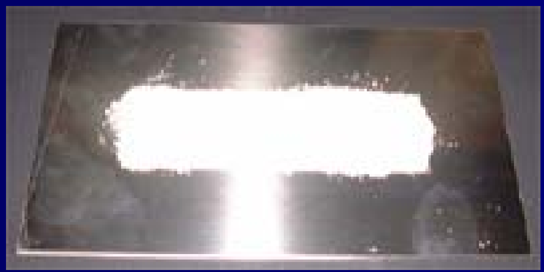
PN

OPE-2Gly(1)

Hardner : Phenol novolac (PN)
Curing condition : 180˚C x 9hr, pressure 2MPa, under vacuum

OPE-2ST(1),OPE-2ST(2)

Hardner : NON
Curing condition : 200˚C x 3hr, pressure 2MPa, under vacuum

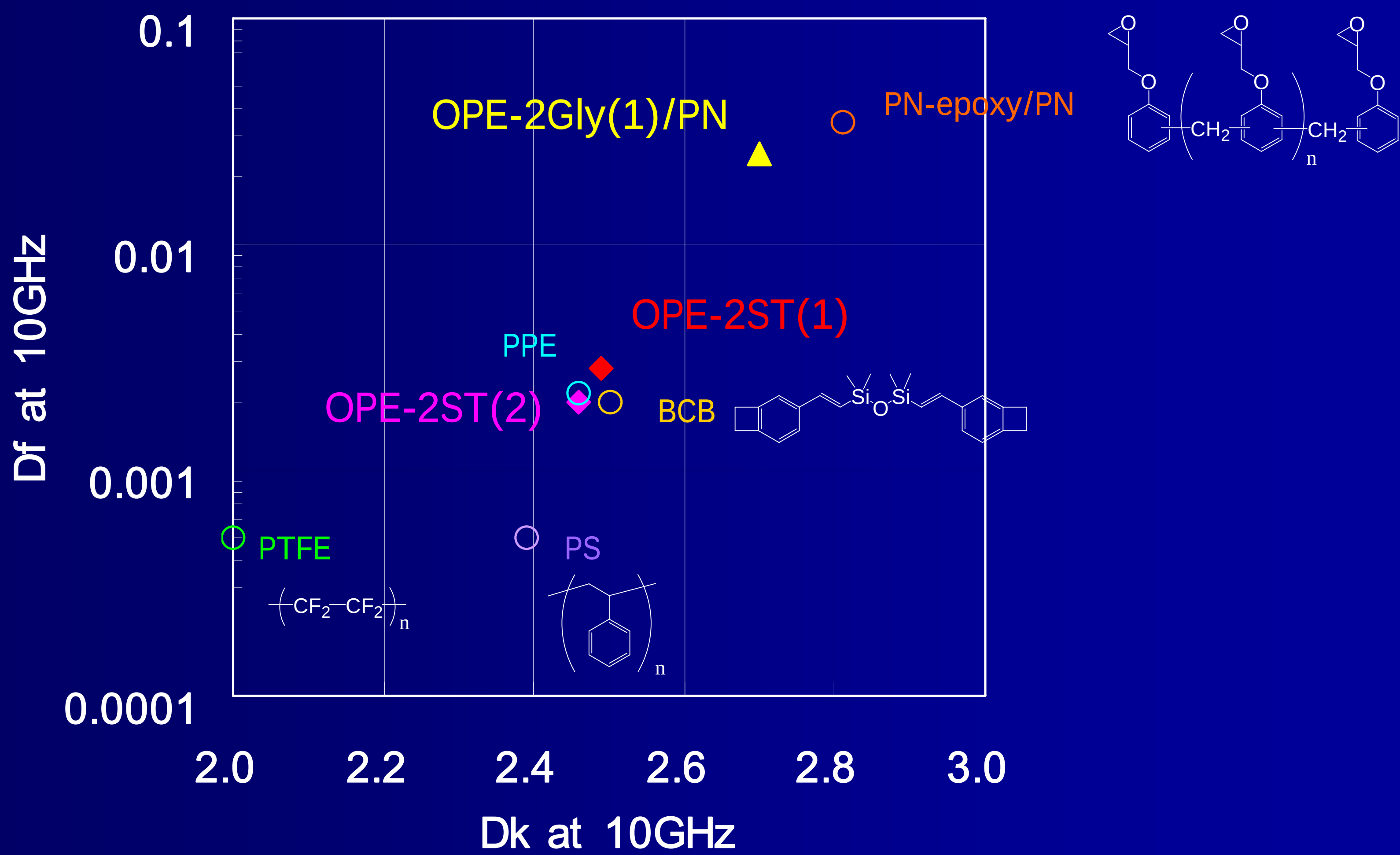


Before curing

After curing

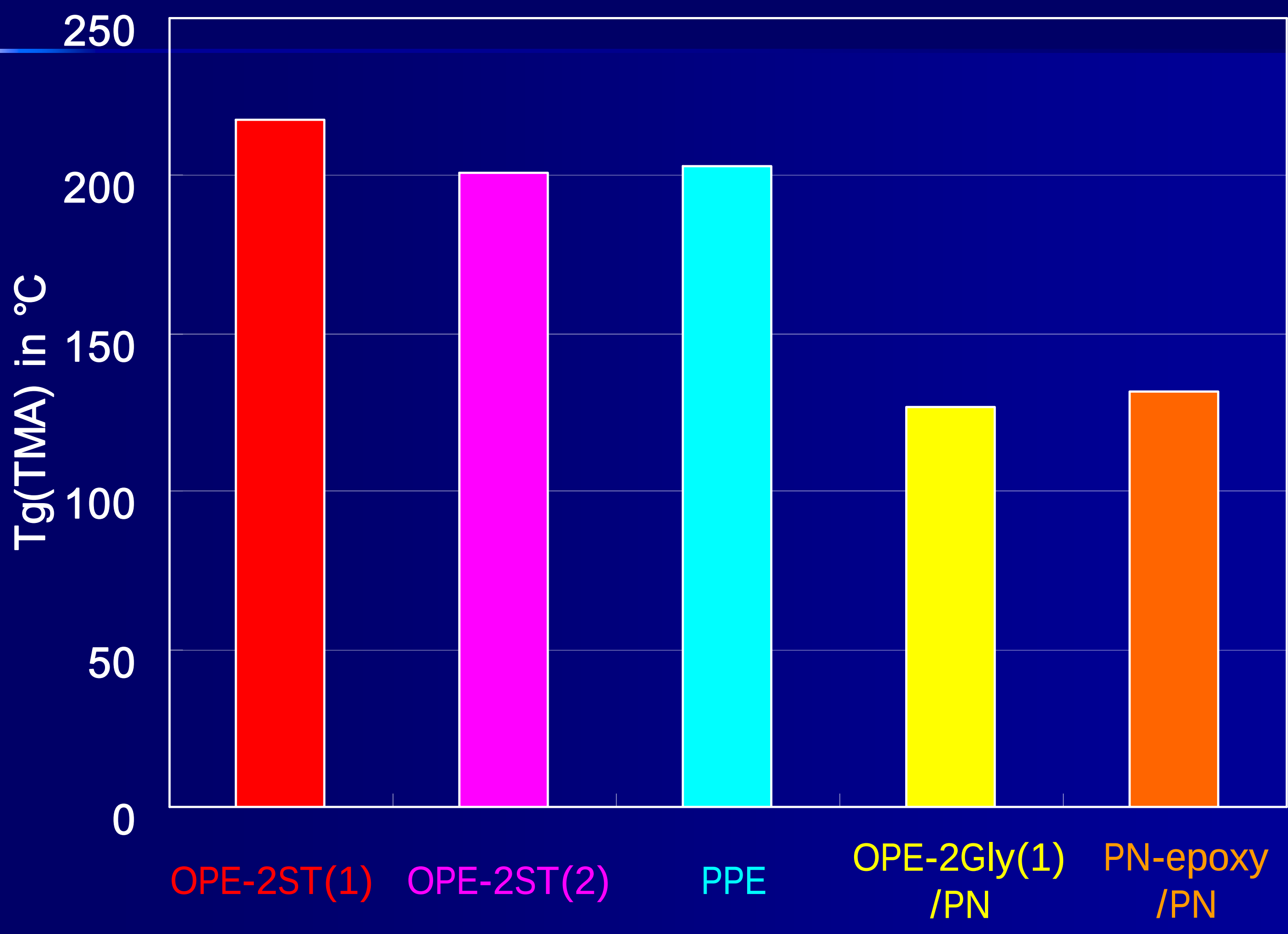
Dielectric properties of cured resins

Perturbation method by cavity resonator

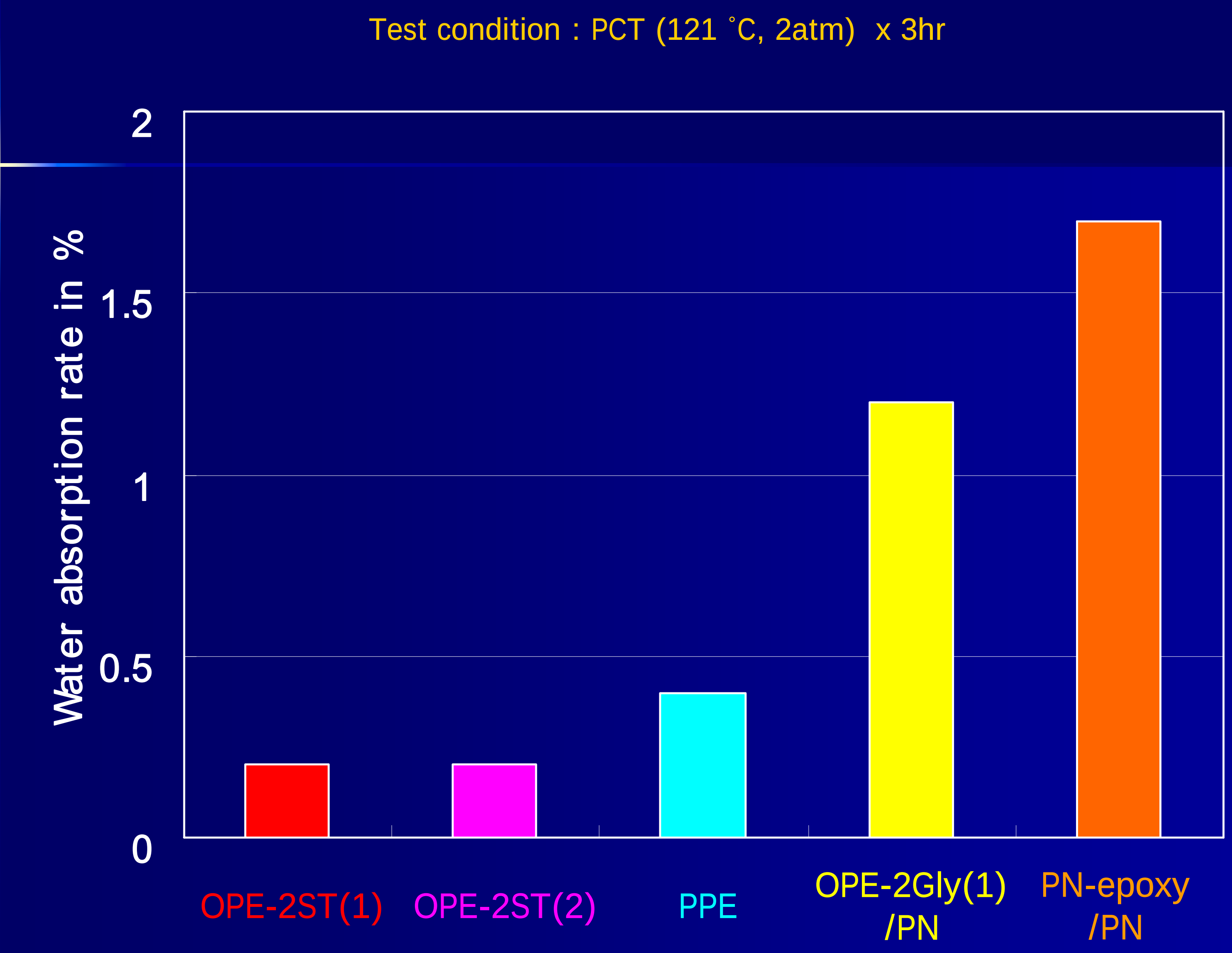


Thermal property of cured resins

Test condition : ramp rate 10 ˚C /min



Water absorption rate of cured resins



Applications of OPE-2ST

OPE-2ST

High-performance

Low Dk (2.5@10GHz)
Low Df (0.002-0.003@10GHz)
High Tg (200-210 ˚C)
Low water absorption rate (0.2%)
Sufficient solubility in organic solvents (>50wt%)

Prospective applications

Insulation film for build-up PWB
Resin coated copper (RCC)
Prepreg
Laminate

Preparation of film by casting method

Cast resin solution onto substrate — Evaporate solvent and cure — Remove substrate

OPE-2ST (no additive)

crack

OPE-2ST/additive

no crack

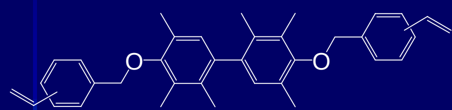
Additives

Styrene-butadiene-styrene copolymer (SBS)

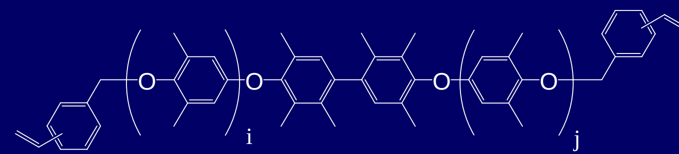
Hydrogenated styrene-butadiene-styrene copolymer (SEBS)

(Low Dk, Low Df, Low water absorption rate, High miscibility with PPE)

Effect of PPE chemistry



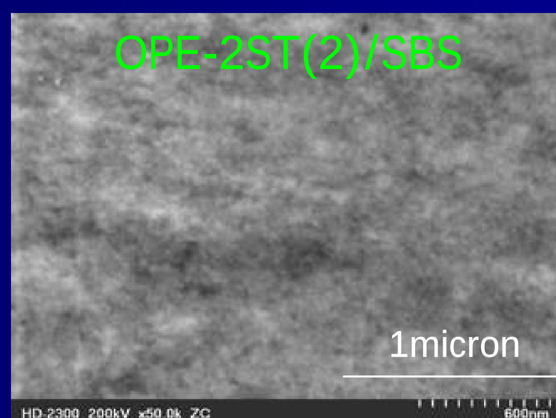
HMBP-2ST
+
SBS or SEBS



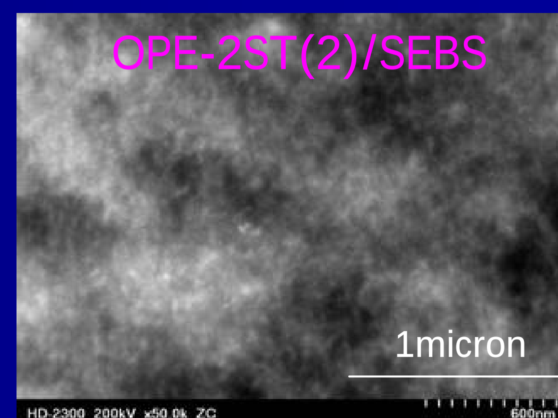
OPE-2ST
+
SBS or SEBS

Macro phase separation

TEM analysis



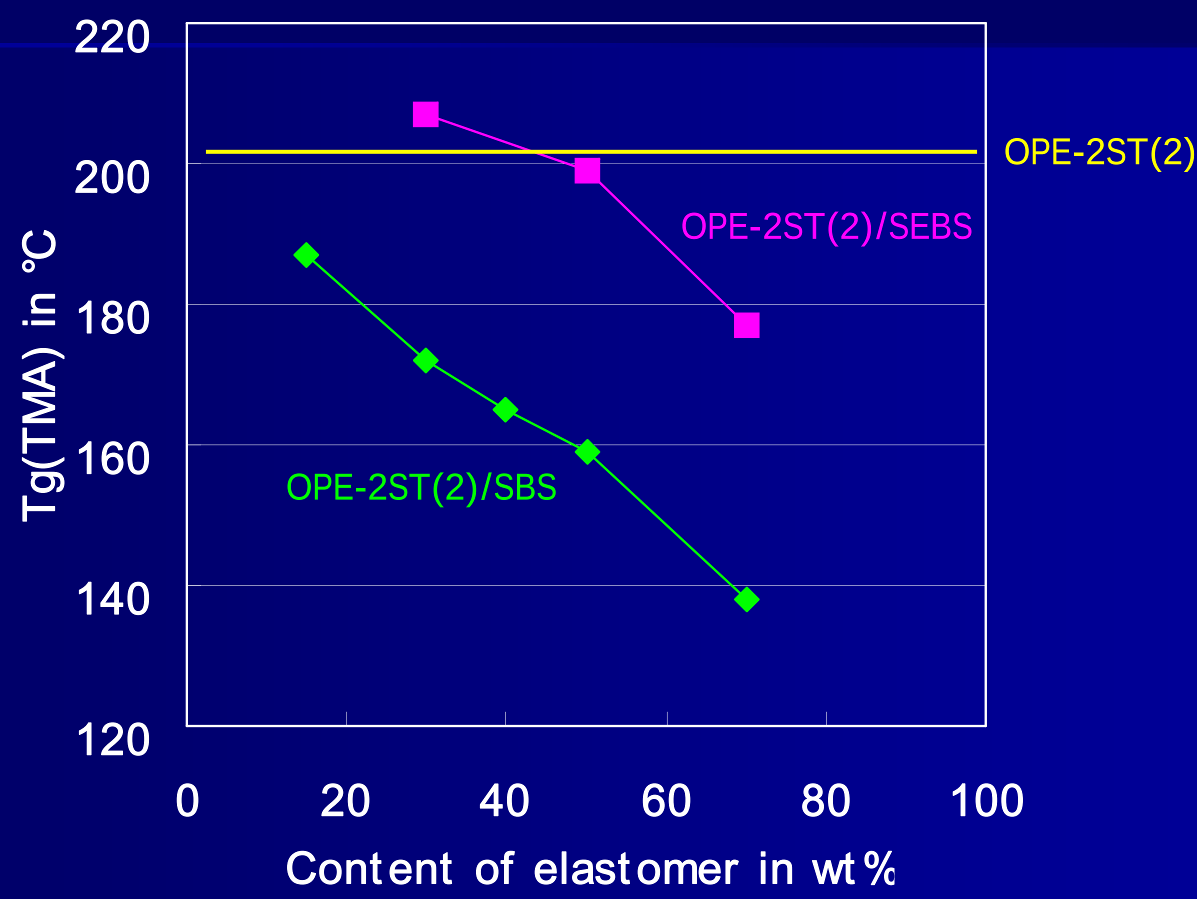
Micro phase separation



Micro phase separation

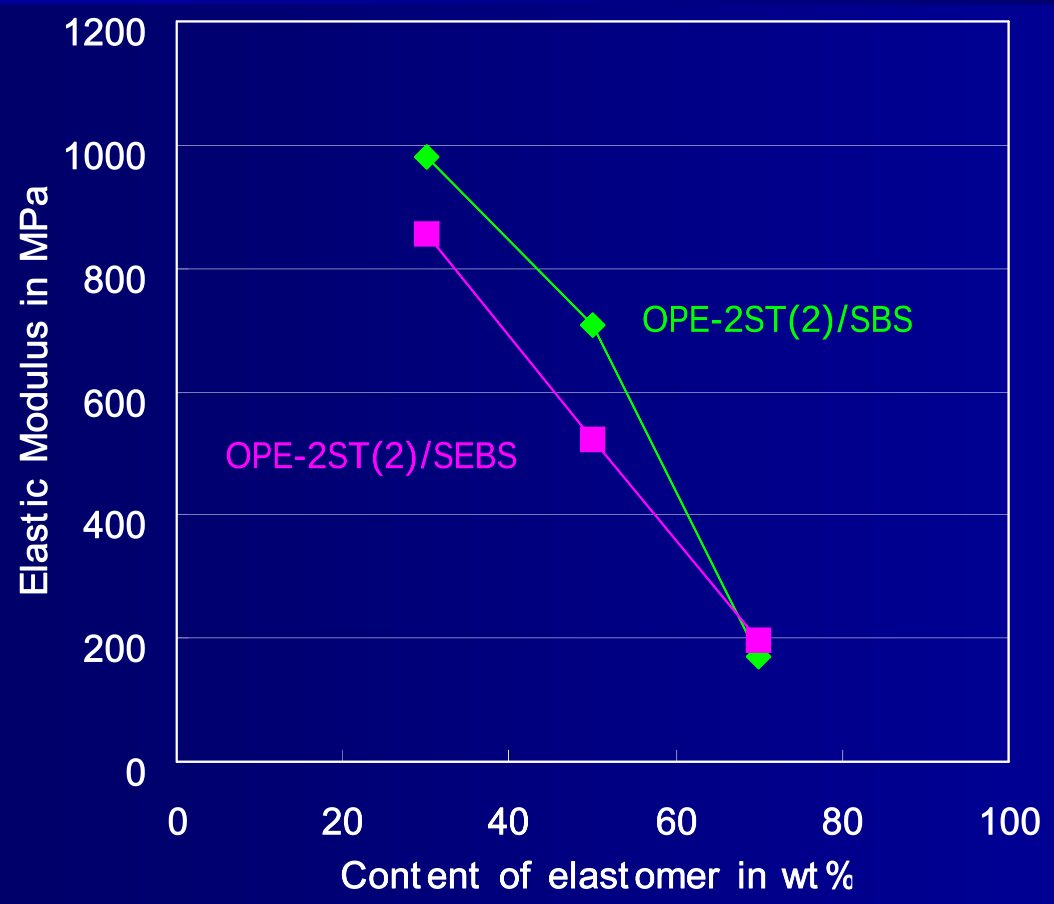
Thermal property of films

Test condition : ramp rate 10 ˚C /min



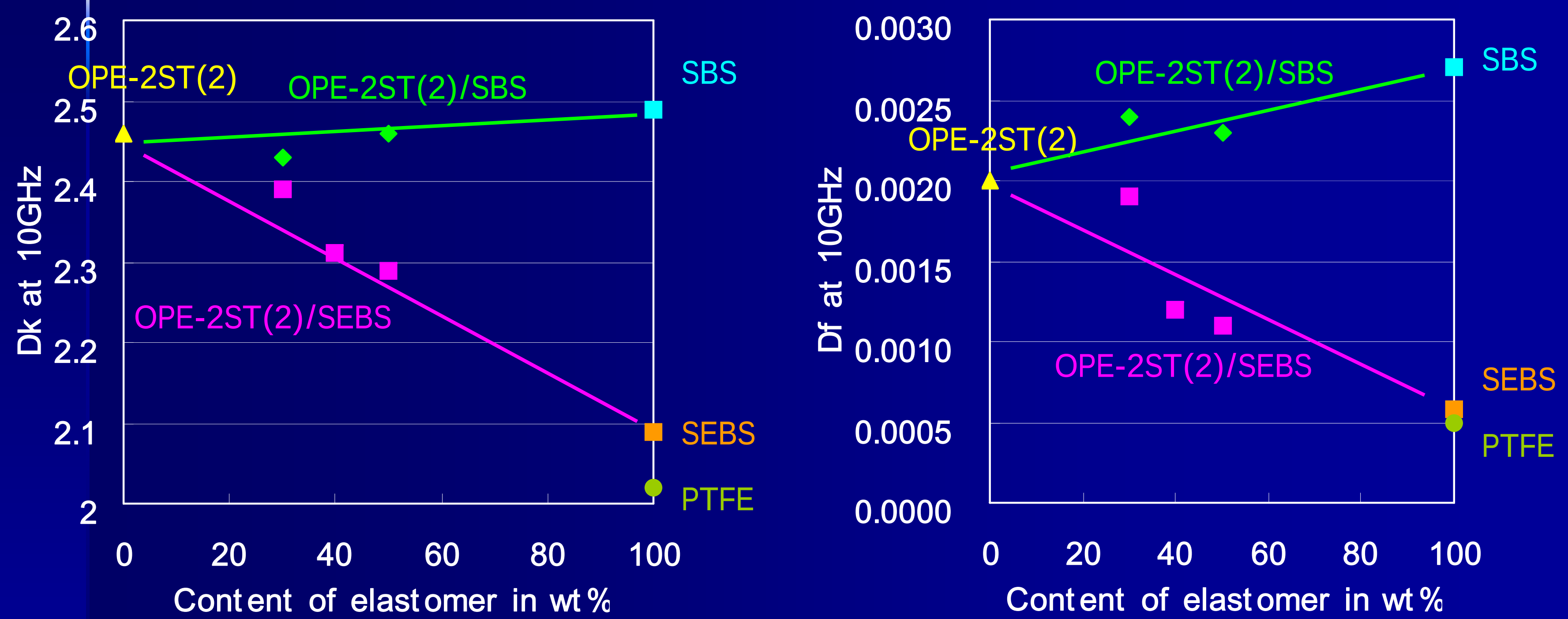
Mechanical property of films

Test condition : speed 100mm/min



Dielectric properties of films

Perturbation method by cavity resonator

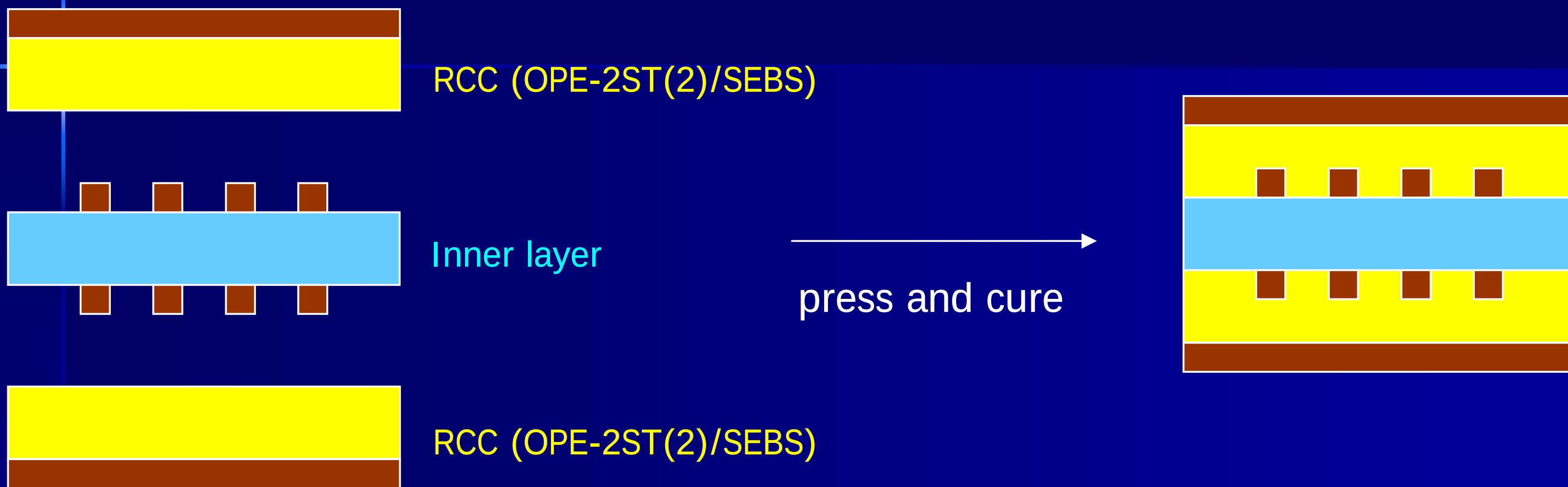


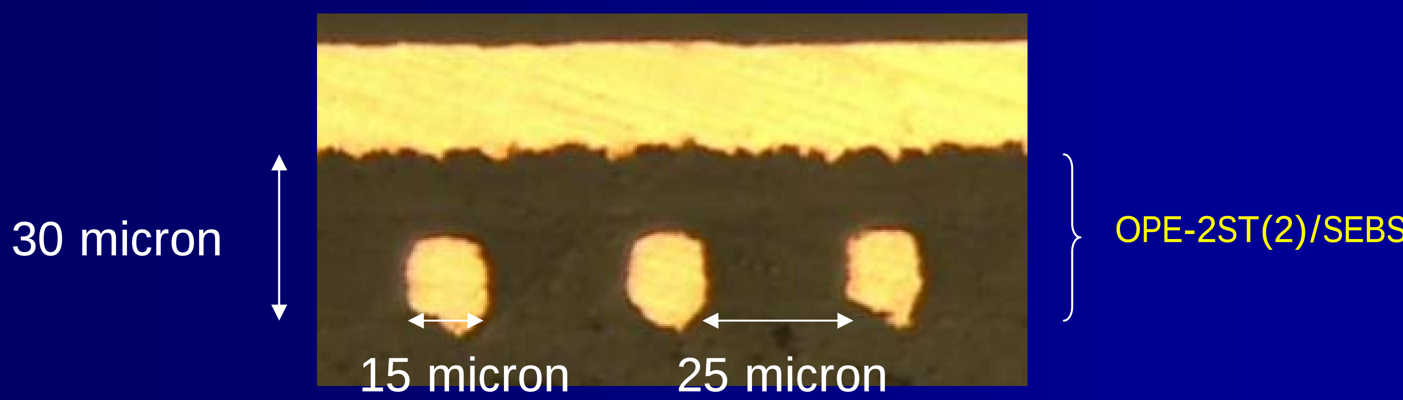
Typical properties of films

Property	Unit		Typical value		Test Method
			Low Modulus	Low Df	
Appearance			light yellow (transparent)		
Electrical					
Dielectric Constant (Dk)	2 GHz	[-]	2.49	2.40	Perturbation method by cavity resonator
	5 GHz	[-]	2.45	2.37	
	10 GHz	[-]	2.42	2.29	
Dissipation factor (Df)	2 GHz	[-]	0.0029	0.0011	
	5 GHz	[-]	0.0027	0.0012	
	10 GHz	[-]	0.0024	0.0011	
Thermal					
Tg	℃		165	188	TMA
CTE	ppm		150	90	TMA
Mechanical					
Elastic Modulus	MPa		226	541	JIS K7127
Stress at Break	MPa		27	34	
Strain at Break	%		37	21	
Folding Endurance	Times		50,000	> 2M	MIT method
	Thickness, micron		40	30	
Chemical					
Water Absorption	%		0.2	< 0.1	Immersed for 1 day at r.t.

Build-up by RCC

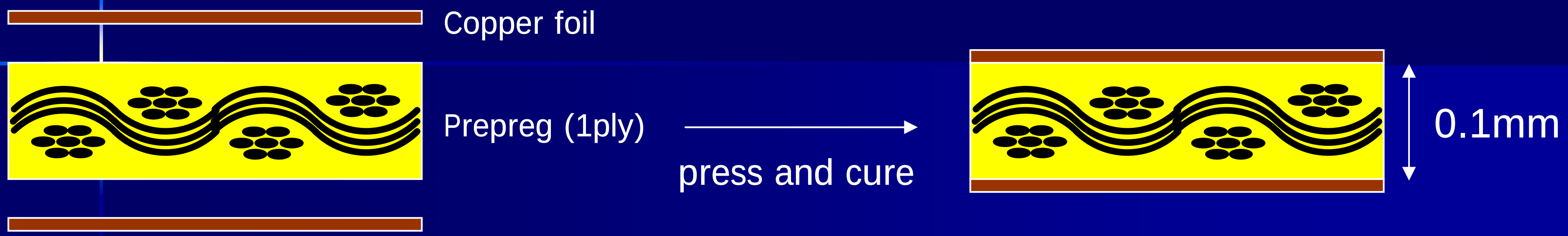
Press condition : pressure 2MPa, ramp rate 3 ˚C /min, temp. 200 ˚C x 90min, under vacuum





Preparation of laminate

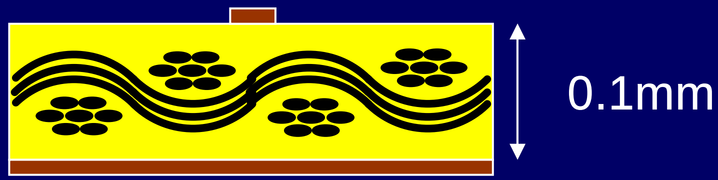
Press condition : pressure 2MPa, ramp rate 3 ˚C /min, temp. 200 ˚C x 90min, under vacuum



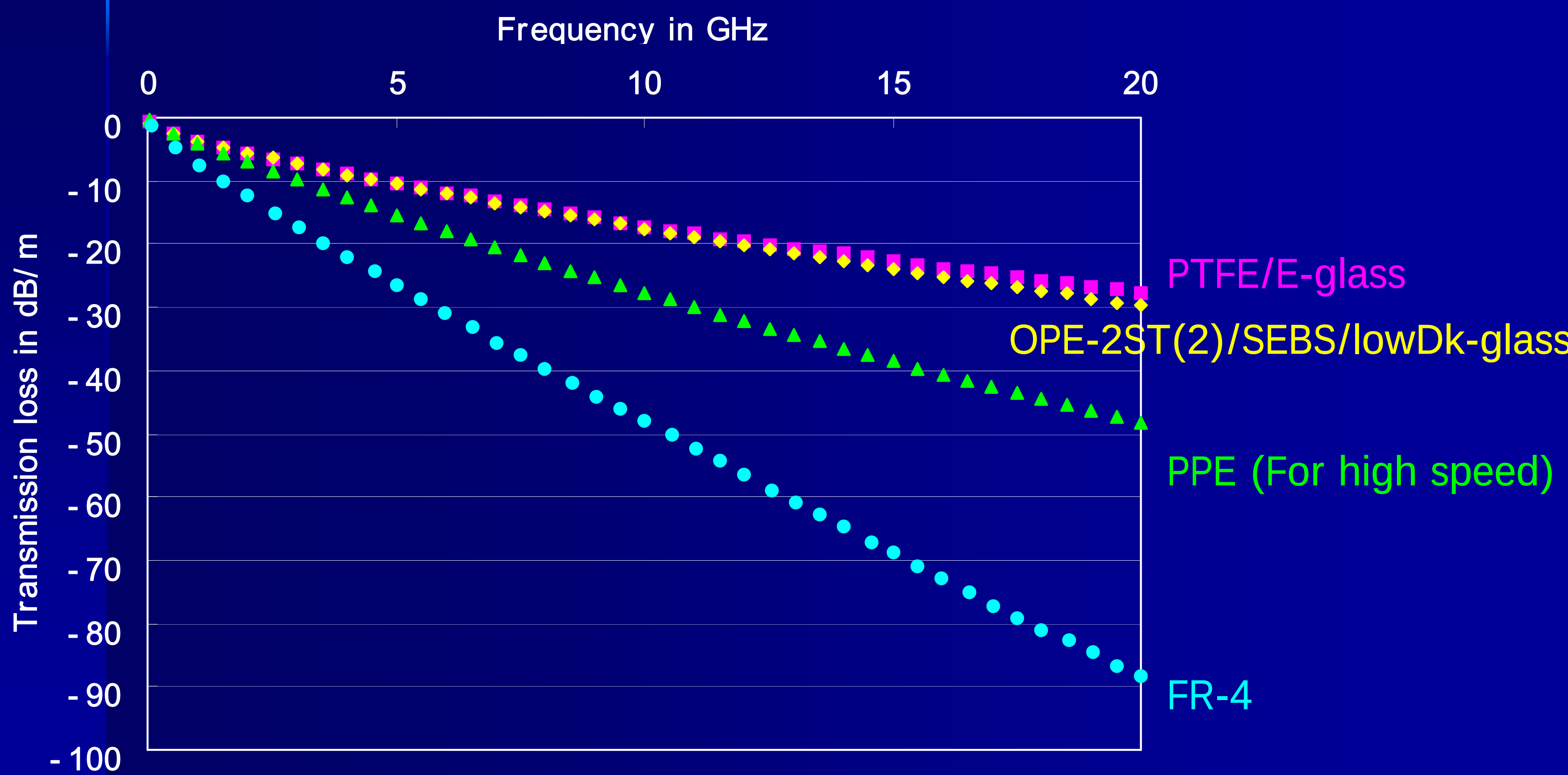
Properties of laminates

Resin system			OPE-2ST(2)/SEBS	PTFE	PPE (For high speed)	Epoxy (FR-4)
Glass fabric			Low Dk	E	E	E
Dk	10GHz	-	2.95	2.45	3.35	3.90
Df	10GHz	-	0.0026	0.0034	0.0041	0.0169
Copper foil peel strength	18μm-thick (low profile)	kN/m	1.1	>1	1.3	1.3
Tg	TMA	˚C	188	<30	190	130
Flammability	UL-94	-	No flame resistance	V-0	V-0	V-0

Transmission loss



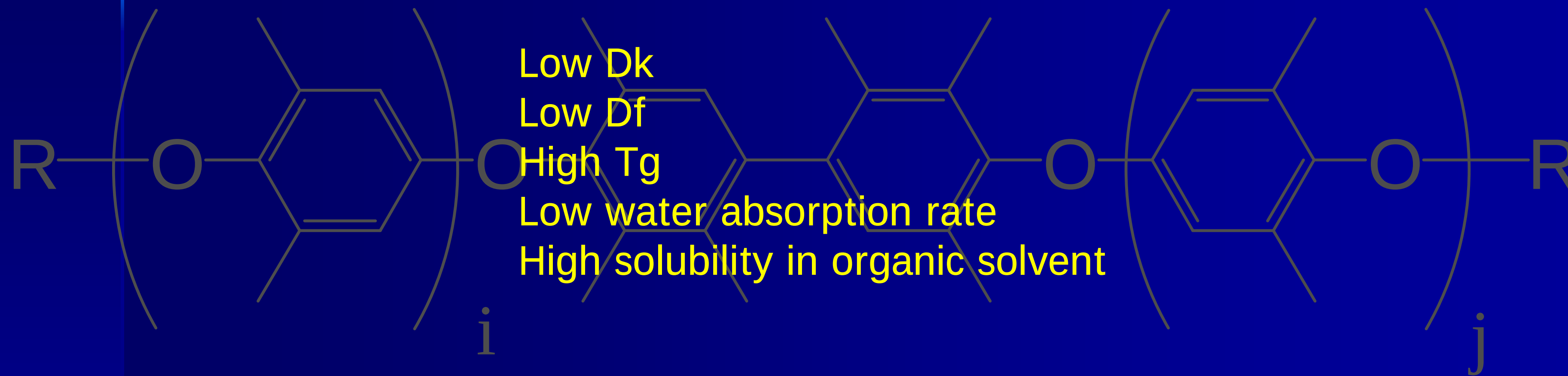
Line length : 300mm
Characteristic inpedance : 50ohm
Copper foil : 18micron



Summary

OPE derivatives

New resins with excellent properties as PWB base materials



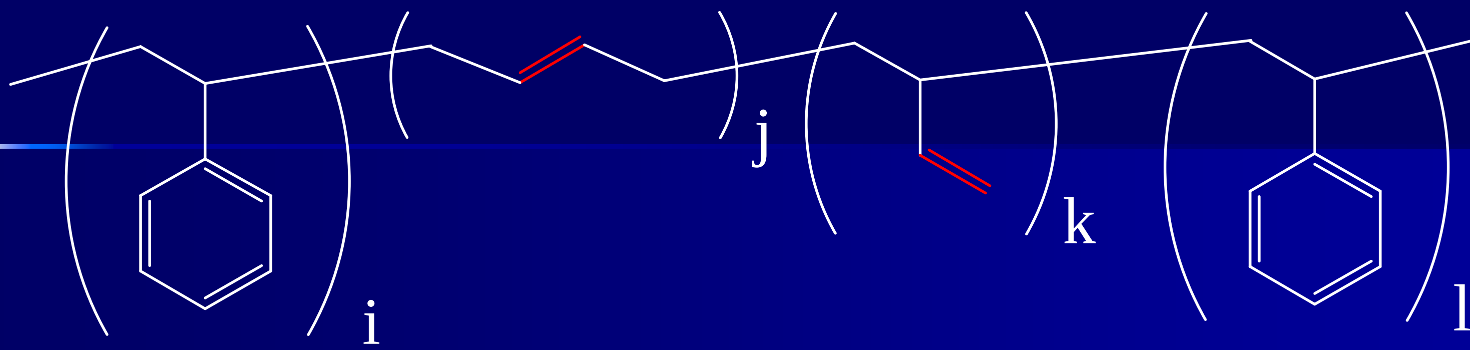
Low Dk
Low Df
High Tg
Low water absorption rate
High solubility in organic solvent

OPE and OPE derivatives will advance and contribute to PWB technology !

Thank you

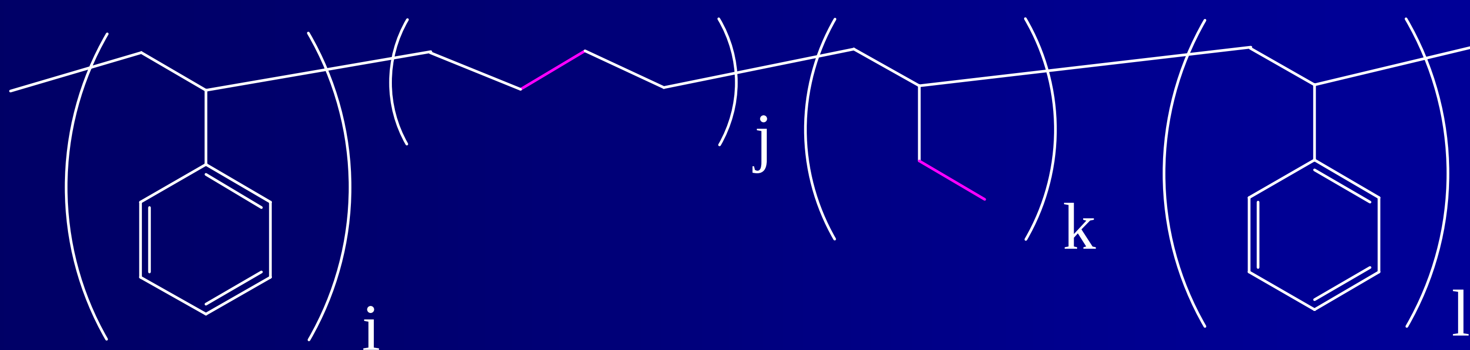
Please visit web site at www.mgc.co.jp/eng/menu.html

Additives



poly-Styrene unit poly-Butadiene unit poly-Styrene unit

Styrene-butadiene-styrene copolymer (SBS)



poly-Styrene unit poly-Ethylene unit poly-Buthylene unit poly-Styrene unit

Hydrogenated styrene-butadiene-styrene copolymer (SEBS)

Properties of laminate (example)

Resin system			OPE-2ST
Glass fabric			Low Dk
Dk	10GHz	-	3.19
Df	10GHz	-	0.0034
Copper foil peel strength	18μm-thick	kN/m	0.85
Tg	DMA	˚C	216
PCT	3hr + solder dipping 260˚C, 60sec	-	OK
Flammability	UL-94	-	V-0

Light transmittance of films