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Unique Allylated Polyphenylene Ether for Low Dielectric Printed Circuit Boards

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For both high speed and high frequency multilayer printed circuit boards, thermosetting allylated polyphenylene ether (A-PPE) was successfully developed by chemically modifying thermoplastic polyphenylene ether (PPE) without sacrificing superior properties of PPE. Its synthesis, properties, are explored and its application to multilayer printed wiring boards is demonstrated.

1. INTRODUCTION

The electronics industry is constantly researching organic materials with low dielectric constant and high glass transition temperature for printed circuit boards[1-3].

Polytetrafluoroethylene (PTFE) is a well-known low dielectric resin. However, PTFE having low glass transition temperature of 25 ℃ is not suitable for high density multilayer printed circuit boards (MPCB) because of its large thermal expansion. in addition, PTFE has poor adhesion to copper foil and must be molded under high temperature and high pressure.

On the other hand, a conventional polyimide is a well known superior heat resistant resin having high glass transition temperature and low thermal expansion and is therefore suitable for MPCB. However, the polyimide with high dielectric constant and dissipation factor is not suitable as MPCB for high speed computers and high frequency devices.

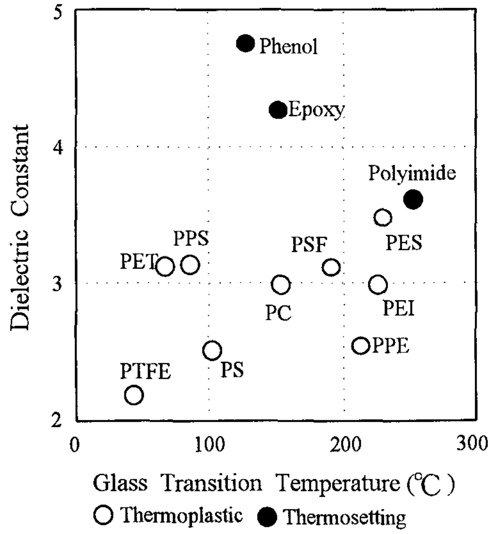
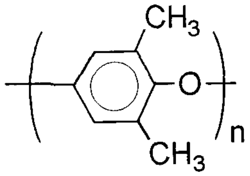


Fig. 1. Dielectric constant and Tg of various resins

In this study, poly(2,6-dimethyl-1,4-phenylene ether) (PPE) was selected in a number of thermoplastic and thermosetting resins shown in Fig. 1 as a low dielectric resin having both low dielectric constant and high glass transition temperature. PPE is soluble in various organic solvents such as halogenated hydrocarbons and aromatic hydrocarbons. Therefore, thermoplastic PPE was chemically modified into thermosetting allylated PPE without sacrificing superior properties, such as low dielectric constant, high glass transition temperature, and low water absorption.

This paper presents the syntheses and properties of allylated PPE converted from thermoplastic PPE via metalation reaction and applications of A-PPE to prepreg, copper clad laminate, and MPCB.

Table 1 Properties of PPE

Poly(2,6-dimethyl-1,4-phenylene ether) :	PPE
	
Dielectric Constant (at 1MHz)	2.4
Dissipation Factor (at 1MHz)	0.0007
Glass transition temp (℃)	210
(trichloroethylene)	soluble

2. ALLYLATED PPE

2.1 Syntheses

For a molecular design to convert thermoplastic PPE into thermosetting PPE, an allyl group was selected as a crosslinkable group. The allyl group has preferable natures listed below.

a. small polarization
b. low crosslinking temperature, similar to epoxy laminate, in the presence of various peroxides
c. no volatile component is produced during crosslinking reaction.

Table 1 shows the properties of PPE used in this Study.

A-PPE was synthesized in the following procedure and the typical reaction scheme was shown in Fig. 2. PPE was metalated in tetrahydrofuran at 40℃ for 30 minute by adding butyllithium in hexane solution under nitrogen atmosphere. The lithiated PPE thus obtained was reacted with allyl halide at 40℃ for 1 hour. A-PPE was precipitated by addition of large quantity of methanol and was dried in vacuum. A-PPE was obtained in powder form. Fig. 3 shows the relationship between the degree of substitution by allyl groups on PPE backbone and butyllithium added. It is indicated that the allylation reaction proceeds almost quantitatively.

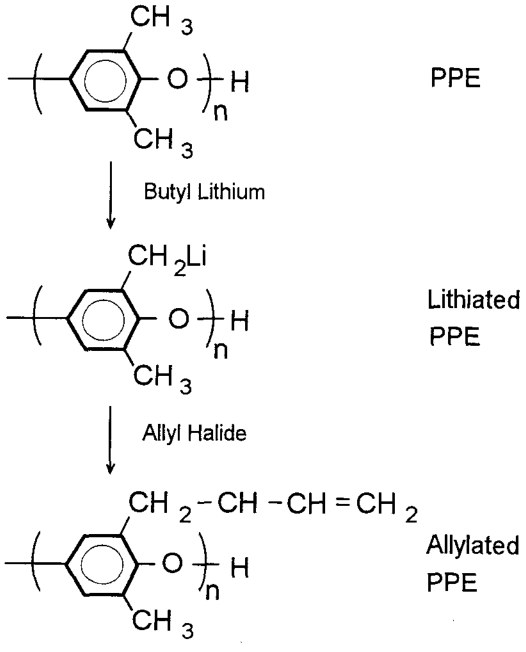


Fig. 2. Synthesis of allylated PPE

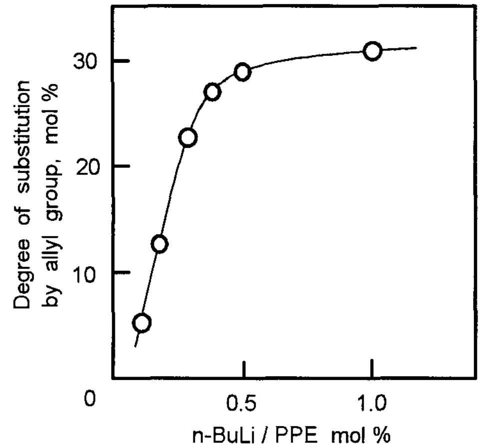


Fig. 3. The dependence of the degree of substitution by allyl group on n-butyllithium

2.2 Properties

A-PPE was thermally cured in the absence of catalyst above the temperature of 250℃. Further study demonstrated that various peroxides accelerated the crosslinking reaction of the double bonds in the allyl groups of A-PPE at low temperatures higher than 150℃. The result is shown in Fig. 4.

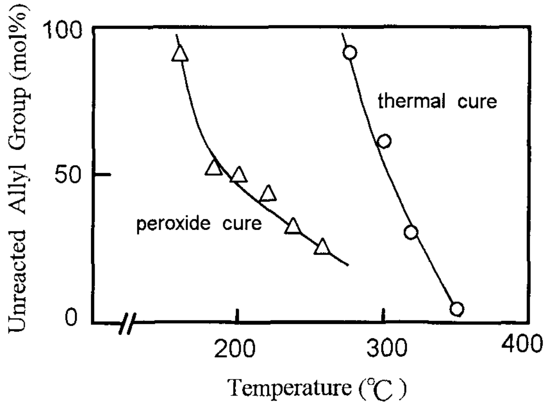


Fig.4 Crosslinking reaction of A-PPE

Table 2 shows the electrical properties, thermal properties, chemical properties, and physical properties of PPE and cured A-PPE. The low dielectric constant of 2.5 and the small dissipation factor of 0.001 of the A-PPE were obtained without sacrificing the excellent dielectric properties of PPE. Further, the cured A-PPE has the low water absorption. The absence of polar functional groups provides the resin having these excellent properties. These characteristics have never beeen matched by conventional thermosetting polymers, such as epoxies, polyimides, and cyanate esters, which cure through reaction of polar functional groups.

The glass transition temperature of the cured resin is higher than that of the original PPE and is comparable to that of polyimide. In addition to the chemical resistance against acids and alkalis, the cured resin is improved in those against halogenated solvents and aromatic hydrocarbons whichin PPE is soluble.

The introduction of allyl groups into PPE provides the favorable properties, such as low dielectric properties, high Tg, low water absorption and mild curing temperatures comparable to the curing temperatures of epoxies. in addition, the A-PPE shows a film-forming property in various solvents, although PPE shows no film forming property in solvents. The A-PPE has excellent adhesion to copper foil without any adhesives. This fact indicates that adhesiveless flexible copper clad laminate can be easily manufactured by A-PPE film and copper foil.

Table 2
Properties of PPE and curedallylated PPE

Property	Condition	Unit	PPE	A-PPE
Electric				
Dielectric constant	1 MHz		2.4	2.5
Dissipation factor	1 MHz		0.0007	0.001
Thermal				
Glass transition temperature(TMA)	10 ℃ /min	℃	210	250
10% Weight Loss temperature	10 ℃ /min	℃	436	420
Solvent resistance				
Trichloroethylene			Soluble	Insoluble
Acid			Insoluble	Insoluble
Alkali			Insoluble	Insoluble
Physical				
Tensile strength		kg/cm^2	730	700
Tensile modulus		kg/mm^2	240	240
Water absorption	23℃,24hr	%	<0.05	<0.05
Peel strength	23℃	kg/cm	NA	1.7
Specific gravity	23℃		1.06	1.06

3. APPLICATION TO LAMINATES

3.1 Prepreg and copper clad laminate

Fabrication of prepreg and copper clad laminate can be done using processes which are common for conventional thermosetting resins. Prepreg is fabricated using a conventional treater. Prior to prepreg fabrication, a peroxide is added to give the resin the required reactivity and to assure a high Tg of cured resin. Prepreg made with A-PPE resin has a quite different property than conventional circuit boards prepreg. The resin on conventional prepreg is brittle, and readily flakes off, leading to contamination problems from resin dust. The prepreg has a film-like property; prepreg resin is more difficult to remove, resulting in far less resin dust.

Copper clad lamination for the resin can be done at temperatures ranging from 170 to 200℃ for 30 minutes to 2 hours in a similar cycle for epoxy laminate. Although most high Tg resins require a postcure, A-PPE requires no postcure. Table 3 compares general properties of A-PPE resin laminate with those of polyimide and FR-4 laminates. The A-PPE prepreg has superior storage stability more than three months at 23℃.

Table 3
Properties of A-PPE, PI, and PTFE laminates

Property	Unit	A-PPE	PI	PTFE
Electric				
Dielectric constant (1MHz)		3.0 - 3.5	4.4 - 4.7	2.5 - 2.7
Dissipation factor (1MHz)		0.002 - 0.003	0.015	0.001 - 0.0015
Thermal				
Glass transition temperature(TMA)	℃	250	260	25
Chemical				
Flammability		V-0	V-1	V-0
Solvent resistance				
Trichloroethylene		Insoluble	insoluble	Insoluble
Acid		Insoluble	Insoluble	Insoluble
Alkali		Insoluble	Decomp	Insoluble
Physical				
Coeffcient of thermal expansion Z-axis	ppm/℃	80-100	40	240
Water absorption	%	0.1 - 0.2	0.3	0.05
Peel strength	kg/cm	1.4 - 1.6	1.2 - 1.6	2.2
Specific gravity		1.44 - 1.64	1.86	2.24

3.2 Multilayer circuit boards

Standard inner layer processing is recommended for A-PPE resin laminate to include oxide treatment to promote copper-prepreg adhesion. Recommended conditions include starting with a press preheated to 180℃ and laminating at 3 MPa for 60 minutes. No postcure is required to develop the highest Tg, not like the conventional high Tg resins. Drilling with standard tungsten carbide drill bit can be accomplished without unusual drill wear. Standard plated through hole processing has been shown to be effective in producing good circuitry. Desmear with a permanganate process has been shown to be effective. Processing through the final stage of MPCB fabrication showed no problem. MPCB's of A-PPE can be produced by a conventional FR-4 process.

40 layer MPCB's were laminated using 0.1mm thick copper clad laminate and 0.050mm thick prepreg made from A-PPE resin and E glass cloth. Reliability of the plated through holes having the diameter of 0.3mm and the aspect ratio of approximately 16 was confirmed by a thermal shock test of 100 cycles between -65℃ and 125℃. As shown by the cross section of through holes in Fig. 4, good reliability of insulation and plated through hole connection is achieved.

4. CONCLUSIONS

Allylated PPE, a new high performance thermosetting resin, has been developed for printed circuit boards applications. This unique resin has a low dielectric contant, a small dissipation factor, high Tg, excellent adhesion to copper foil and low water absorption.

Laminates which consist of A-PPE resin and E glass cloth have low dielectric constants, small dissipation factor, high Tg, and conventional processability comparable to FR-4.

MPCB's with 40 layers were fabricated using the A-PPE laminates and prepregs, and their practical reliability was confirmed.

This new resin should be of great value in high speed /high frequency printed circuit board applications. It should be also useful in applications which require good thermal properties, low water absorption, and good adhesion to copper foil.

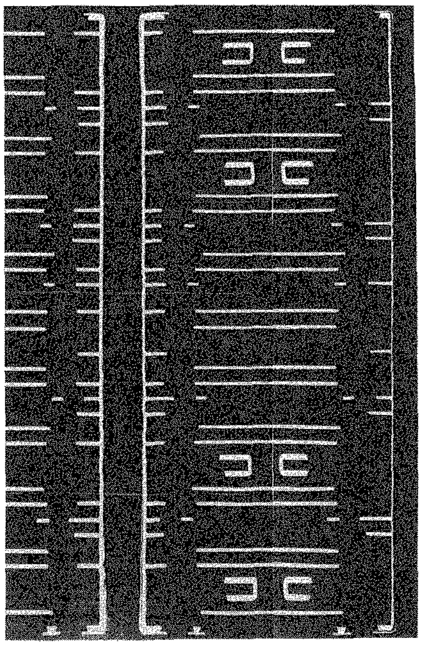


Fig. 6. Cross section of through holes ofMPCB with 40 layers after heat-shock cycles

5. ACKNOWLEDGEMENT

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