

Preparation of Poly(2,6-Dimethyl-1,4-Phenylene Ether) (PPE)/Epoxy Laminate with Functionalized PPE Resin

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SYNOPSIS

Thermal expansion property at 288°C and methylene chloride resistance of poly(2,6-dimethyl-1,4-phenylene ether (PPE)/epoxy laminate were found to be affected by the functionality on PPE resin. Nonlofting PPE/epoxy laminates were prepared with the PPE grafted with fumaric acid or the PPE having (*di-n*-butylamino)methyl substituent on the polymer backbone. Employing vacuum-vented PPE extrudate or phenol-redistributed PPE was also effective in improving the PPE/epoxy laminate properties. Attempts to preparing a real PPE/epoxy interpenetrating network as the matrix material for the laminate were also made by incorporating both PPE crosslinker and epoxy curing catalysts in the same formulation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

High molecular weight poly(2,6-dimethyl-1,4-phenylene ether) (PPE) resin was found to be miscible with 4,4'-isopropylidenediphenol diglycidyl ether (BPADGE) at elevated temperature. The resulting mixture could be cured with added curing catalysts. Preliminary results indicated that the cured PPE/epoxy blends had excellent physical, chemical, and electrical properties. This intriguing combination of properties suggested application as a matrix material for circuit boards.¹

Methylene chloride resistance and low solder expansion are two of the preliminary tests the cured PPE/epoxy laminate has to pass in order to be qualified for printed circuit board applications. Since solvents based on methylene chloride are commonly used to remove the patterned resist in the manufacture of printed circuit boards, it is essential that the base laminate is not damaged in the process. The methylene chloride resistance test measures the weight and surface change after the laminate has been dipped in methylene chloride for 30 min and then air dried for 10 min. The conventional pure epoxy board (FR-4) has only 1.1% weight gain and

maintains a very smooth surface after the methylene chloride test. Printed circuit boards, like any other materials, change their sizes with changes in temperature. The resin is the least dimensionally stable component of the laminate, and its movement with changes of temperature is constrained by the glass reinforcement. Moreover, *Z* plane expansion in board laminate is always significantly greater than *X* and *Y* plane expansion because there is no continuity of reinforcement through the thickness of the boards. This can cause problems on all types of boards.² Thus, the solder test measures the change in the laminate thickness (*Z*-axis expansion) with a caliper after the laminate is immersed in the 288°C solder bath for 30 s and then cooled to room temperature. The FR-4 board has < 1% *Z*-axis expansion in the solder test. To sell PPE/epoxy laminate as a premium product, we certainly want the testing results on the new laminate to be equal or better than those of the FR-4 board despite the fact that the new board will have a higher glass transition temperature, T_g , because of the presence of PPE resin.

Hobbs and Watkins³ reported that over the PPE/epoxy composition range 20/80–80/20, the blend phases separate on curing to form dispersed epoxy domains imbedded in a continuous PPE matrix. Since methylene chloride is known to be a solvent for PPE, the PPE in the continuous phase of PPE/

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epoxy laminate has to be chemically linked to the crosslinked epoxy phase in order to survive the methylene chloride test. Further, the PPE/epoxy copolymer is expected to improve the adhesion and compatibility between PPE and crosslinked epoxy phases. As a result, the thermal expansion, that is, solder resistance, of the laminate may also be improved because of the copolymer presence. In this report we summarize the findings on how the laminate's solvent resistance and thermal expansion are affected by replacing virgin PPE with modified PPE in the resin formulation.

EXPERIMENTAL

All commercially available compounds were used as received without further purification. Epon 828 (4,4'-isopropylidenediphenol diglycidyl ether) was purchased from Shell Chemical Co. PPE (0.46 or 0.40 intrinsic viscosity, i.v.) was obtained from GE Noryl Products, Selkirk, New York. Epn 1138, an epoxy phenol novolac resin, and HT-9490, a phenolic hardener, were purchased from Ciba-Geigy Corporation. Woven glass cloth (Burlington, #2116, 0.07047 g/in²) was used in the preparation of pre-pregs. Gel permeation chromatography (GPC) was performed in an HP 1090 liquid chromatograph with a UV detector at 254 nm. The eluent used was chloroform containing 0.5% (v/v) absolute ethanol. The oven temperature for the GPC column was maintained at 40°C, and the flow rate was set at 1 mL/min. The column, a PLgel 5 micron mixed packing with the dimension of 300 × 7.5 mm, was purchased from Polymer Laboratories. The calibration curve was established with a few known molecular weight polystyrene standards. Fourier transform infrared spectra (FTIR) were obtained from a Nicolet 7199 spectrophotometer at one wavenumber resolution. The sample solution was made by dissolving 127.2 mg of PPE or modified PPE in 5 mL of CS₂. The IR carbonyl absorbance of the modified PPE was obtained by subtracting the unmodified PPE spectrum from the sample spectrum. PPE hydroxy content (wt %) was estimated from the absorbance at 3610 cm⁻¹. NMR spectra were obtained with a Nicolet QE-300 (¹H NMR, 300 MHz) spectrometer relative to an internal tetramethylsilane standard. Differential scanning calorimetry (DSC) measurements were made on a Perkin Elmer Series 7 DSC differential scanning calorimeter with a scan rate of 20°C/min. Thermal gravimetric analysis (TGA) of the polymer was obtained using a Dupont 9900

thermal analyzer equipped with the 951 thermal gravimetric analyzer. All the *T_g* data of the laminates were obtained via dynamic mechanical analysis (DMA). The analysis was made on a duPont Model 1090 thermal analyzer equipped with the 982 DMA module or an RDS Dynamic Spectrometer manufactured by Rheometrics, Inc. The GC analysis was performed on an HP 5890 gas chromatograph using a Supelco SPB-1 (30 m, 0.32 mm i.d.) column with a Shimadzu C-R3A integrator, and the sample was derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide first before injection.

Model Reaction of Mesityl (3) and Phenylglycidyl Ether

Mesityl (1.36 g, 0.01 mol), phenylglycidyl ether (1.5 g, 0.01 mol), and *N,N*-dimethylbenzylamine (0.13 g, 1 mmol) were heated at 120°C for 2 h. The adduct **4** was formed in quantitative yield by GC analysis.

Model Reaction of 2,4-Dimethyl-6-(*di-n*-butylamino)methylphenol (5) and Phenylglycidyl Ether

Phenylglycidyl ether (1.5 g, 10 mmol) and 2,4-dimethyl-6-(*di-n*-butylamino)methylphenol (**5**) (2.62 g, 10 mmol) were heated at 120°C for 3 h, and no reaction occurred between them. The reaction temperature was then raised to 160°C, and many products were formed in 3 h. After stirring overnight at 160°C the phenylglycidyl ether was completely consumed, and a small amount of **5** (< 10%) was still in the reaction mixture containing more than 20 components by GC analysis.

Preparation of Fumaric Acid-Grafted PPE

Fumaric acid was first mixed with 500 g of plant PPE resin in a blender until an even dispersion was achieved. The actual grafting was performed in a 28-mm WP intermeshing, self-wiping twin screw extruder of 27 : 1 length to diameter ratio with the standard Noryl compounding screw configuration. The screw turned at 317 rpm and the blend was fed into the extruder at a rate of 5–8 lb/h. The extruder was not vented and all the zones were heated to 300°C, with the exception of zone 1 being heated to 150°C. The extruder was purged with plant PPE resin initially. The fumaric acid-grafted pellets were dried at 60°C overnight before use.

Three batches of fumaric acid-grafted PPE with 1X, 2X, and 3X concentration of fumaric acid load-

ing were prepared. The batch with 2X concentration of fumaric acid was used in preparing PPE/epoxy resin formulation. The concentration "X" is defined as the number of moles of fumaric acid charged relative to one mole of PPE polymer having a number average molecular weight of 15,000.

Preparation of *Di-n*-Butylamine-Modified PPE

A procedure reported by White and Nye⁴ was followed. The PPE (144.0 g) was first treated with *N*-bromosuccinimide (53.4 g, 0.40 mol) in carbon tetrachloride (1500 mL) at reflux for 4 h. The reaction mixture was filtered while hot and the polymer was precipitated by adding the filtrate to methanol in a blender. The precipitate was washed with methanol thoroughly and dried in a vacuum oven overnight at 60°C to form the PPE containing the α -bromo unit. The brominated PPE in toluene (1200 mL) was then treated with *di-n*-butylamine (80 mL) at room temperature for 18 h. The PPE containing α -*di-n*-butylamino unit was precipitated from methanol. From NMR integration, every 10 PPE repeating unit has one unit containing one α -*di-n*-butylamino functionality.

Preparation of Resin Formulations Using Virgin PPE, Modified PPE, or Vacuum-Vented PPE Extrudate

To a 5-L three-necked flask, equipped with a mechanical stirrer, a condenser, and a thermometer, were added toluene (2500 mL) and PPE or modified PPE (630.0 g). The flask was heated to 85°C until a homogeneous solution was formed. Epon 828 (270.0 g), aluminum acetylacetonate (27.0 g), and 1,1,3,3-tetramethylguanidine (5.0 g) were then added sequentially. After stirring for another 15 min, the solution was transferred to a 1-gallon jug to be used in the treater immediately.

Preparation of Resin Formulations Using Redistributed PPE

To a 5-L three-necked flask, equipped with a mechanical stirrer, a condenser, and a thermometer, were added toluene (2500 mL), PPE (630.0 g), and BPA (6.3 g) or HT-9490 (6.3 g). The flask was heated to 90°C until a homogeneous solution was formed before adding 3,3',5,5'-tetramethyldiphenylquinone (TMDQ, 6.3 g). The mixture was stirred at 90°C for 2 h to complete the PPE redistribution reaction. Epon 828 (270.0 g), aluminum acetylac-

tonate (27.0 g), and 1,1,3,3-tetramethylguanidine (5.0 g) were then added sequentially. After stirring for another 15 min, the solution was transferred to a 1-gallon jug to be used in the treater immediately.

Attempts to Prepare Redistributed PPE Containing Carboxylic Acid Functionality

To a toluene solution of PPE (0.40 i.v., 60.0 g) was added salicylic acid (1.2 g) at 95°C. After a homogeneous solution was formed, benzoyl peroxide (1.2 g) was added to the mixture. The reaction was stirred at 95°C for two more hours to complete the redistribution process. The polymer was precipitated with methanol in a blender. In addition to salicylic acid, the equilibration reactions of PPE were attempted using *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, methyl salicylate, methyl *m*-hydroxybenzoate, and methyl *p*-hydroxybenzoate.

Prepreg Formation

The resin solution was placed in a heated dip tank with no circulation. The 12" glass cloth passed through the dip tank in a preset speed to carry the proper amount of resin with it. The resin-coated cloth rose through the steam-heated oven where most of the toluene was removed. The dried prepreg was then cut to convenient sizes for pressing. The resin content of the prepreg is determined by the cloth speed, the dip tank temperature, and the solid content of the solution. Usually 40–44% resin content in the prepreg is considered acceptable.

Preparation of Laminates

The prepreg was further dried in a convection oven (150–180°C) to ensure complete removal of solvent. The prepreg was then cut into suitable size panels and ten panels were used for each laminate. The stack of 10 prepreps was pressed in a four post Wash Hydraulic Press against fluorocarbon-sprayed ferro plates for 50 min at 240°C and 400 psi to yield a laminate.

Z-Axis Expansion

A strip of laminate (1" × 2") is immersed in a solder bath at 288°C for 30 s. The sample is taken out of the bath, cooled, and the excess solder on the tested sample is scraped off. The difference in thickness before and after the test is measured with a caliper, and recorded as the percentage of the original thick-

ness. A nonlofting sample usually maintains its translucency before and after the test. A lofted sample often turns opaque after the solder test.

Solvent Resistance

A piece of laminate (2" × 2") is soaked in methylene chloride for 30 min. It was then air dried for 10 min. The weight difference before and after the test is recorded as the percentage of the original weight. The sample is then placed in a heated (70°C) vacuum oven overnight to remove the absorbed solvent. Again, the weight change of the oven-dried sample from its untested form is recorded as the percentage of the original weight.

Screening of Potential PPE Crosslinkers

PPE (1.0 g) powder and the crosslinker candidate (0.1 g) were mixed thoroughly with a stirring rod. The resulting mixture was then compression-molded between two teflon-coated sheets at 270°C for 1 min. The molded film was cut into small pieces and suspended in chloroform with stirring for 4 h. The insoluble material was filtered, dried, and the yield calculated.

Reaction of PPE and Peroxides in Solid State

PPE (30.0 g) was dissolved in toluene (270.0 g) to form a homogeneous solution. To the mixture (10.0 g) was added peroxide (0.1 g, 1 wt % based on PPE), and the resulting mixture was cast on a glass slide to form a thin film. The thin film was first dried in a vacuum oven at room temperature for 1 h, and then placed in a convection oven at 240°C for 30 min. After the slide was cooled, it was immersed in warm chloroform to examine the PPE film's solubility.

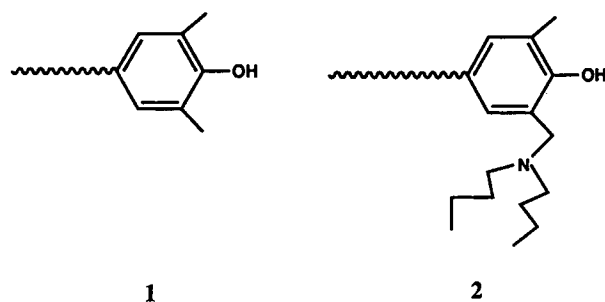
Preparation of Resin Formulations Using PPE and PPE Crosslinkers

To a 5-L three-necked flask, equipped with a mechanical stirrer, a condenser, and a thermometer, were added toluene (2500 mL) and PPE (630.0 g). The flask was heated to 85°C until a homogeneous solution was formed. Epon 828 (270.0 g), aluminum acetylacetonate (27.0 g), 1,1,3,3-tetramethylguanidine (5.0 g), and the crosslinker (37.8 g, 6 wt % based on PPE) were then added sequentially. After stirring for another 15 min, the solution was transferred to a 1-gallon jug to be used in the treater immediately.

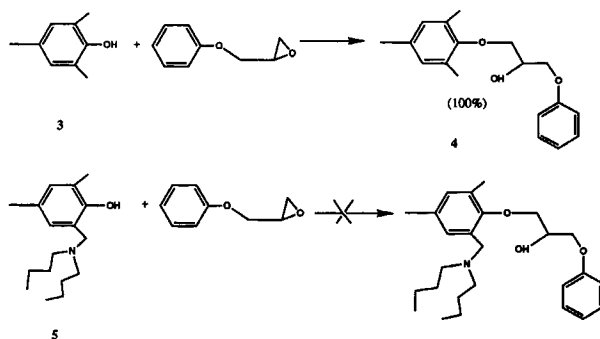
RESULTS AND DISCUSSION

Model Reactions of PPE End Groups and Epoxy

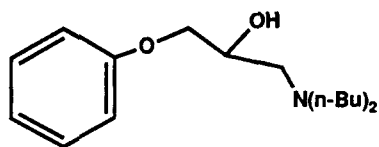
The virgin PPE has two types of phenolic end group: the regular 2,6-dimethylphenol **1** end and the Mannich-type 2-methyl-6-(*di-n*-butylamino)methylphenol **2** end⁴ in a molar ratio of 3 : 2.^{5,6} A model compound study found that mesitol (**3**), the model for end



group **1**, reacted with phenylglycidyl ether in the presence of an amine catalyst to give the adduct **4** in a quantitative yield (Scheme 1). However, the Mannich end model, 2,4-dimethyl-6-(*di-n*-butylamino)methylphenol (**5**), decomposed slowly at 160°C before any significant reaction with phenylglycidyl ether could occur (Scheme 1). The only identified product in the mixture was the reaction adduct **6** between *di-n*-butylamine and phenylglycidyl ether. The *di-n*-butylamine presumably was derived from the thermal decomposition of **5**. The addition of *N,N*-dimethylbenzylamine as the catalyst at the beginning did not improve the reaction, and still gave numerous products. Thus, it seemed reasonable to assume that with unmodified PPE most of the PPE-epoxy copolymer in the laminate would be generated by reacting **1** with the epoxy components. The PPE molecules possessing the Mannich type group **2** as its only phenolic end group would have difficulty in forming copolymer with epoxy.



Scheme 1

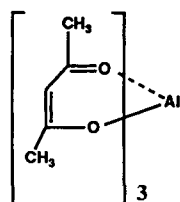
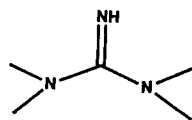


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A formulation with 70/30 (by weight) PPE/epoxy ratio was used throughout the studies. If the laminate properties, such as methylene chloride resistance and *Z*-axis expansion, are tied to the functionalities of PPE, using such a high PPE content in the resin should amplify their effects.

Virgin PPE

A control experiment was conducted by using virgin PPE with 0.46 i.v. and Epon 828. The latent catalyst package⁷ employed to cure the system was a combination of aluminum acetylacetonate ($\text{Al}(\text{acac})_3$), and 1,1,3,3-tetramethylguanidine (TMG).

 $\text{Al}(\text{acac})_3$ 

TMG

Fifty minutes at 240°C was needed for the laminate to reach a steady state in which no further curing reaction was observed. The resulting laminate had one major T_g at 187°C and one minor T_g at 223.2°C. The lower T_g clearly indicated the PPE phase was plasticized by epoxy. It gained 11% of its original weight in the solvent test. After overnight drying to remove the absorbed methylene chloride, it lost 3% of its original weight and had an eroded surface caused by the dissolution of PPE in methylene chloride. The tested coupon expanded 13% of its original thickness after a solder dip test. Apparently the laminate derived from virgin PPE and epoxy failed both tests.

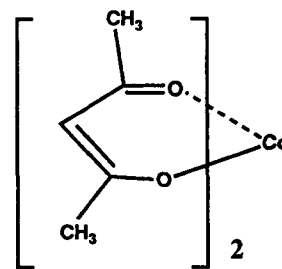
Modified PPE

It is known that carboxylic acid, amine, and phenolic functionalities react with epoxide in the presence of a base catalyst to form the adducts through the ring opening of epoxide. Using PPE modified with one of those functionalities should facilitate the PPE/epoxy copolymer formation during lamination.

Comparing the laminates derived from virgin PPE and those made from modified PPE, we may be able to gain some insights into the relationship between copolymer content and the laminate's properties.

Fumaric Acid-Grafted PPE

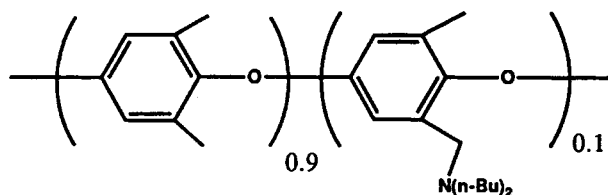
Fumaric acid-grafted PPE was obtained by coextruding PPE powder with fumaric acid.⁸ The resulting pellets were used directly in preparing the PPE/epoxy formulation without purification. The grafting reaction was by no means a clean reaction; several carbonyl absorptions were observed in the FTIR spectrum, and they were difficult to resolve and quantify. Using the fumaric acid-grafted PPE instead of virgin PPE in the same formulation as the control experiment, we made a laminate with only 0.8% *Z*-axis expansion that was close to the FR-4 epoxy board. The solvent intake after the methylene chloride test also improved to 6.2%. Better yet, the sample lost only 0.1% of its original weight after driving out the absorbed methylene chloride, and the surface of the dried laminate was quite smooth. It had two T_g 's at 120 and 212°C representing the epoxy and PPE phases, respectively. This was the first example for which we demonstrated that the improvement of the PPE/epoxy copolymer formation might have significant effect on the properties of the laminate. Using cobalt (II) acetylacetonate⁹ ($\text{Co}(\text{acac})_2$) instead of $\text{Al}(\text{acac})_3$ with fumaric acid-grafted PPE also gave a laminate with no *Z*-axis expansion, similar solvent resistance property, and a PPE phase T_g at 213°C.

 $\text{Co}(\text{acac})_2$

The extra extruder-grafting step to producing a carboxylic acid-modified PPE was demonstrated to be essential for the nonlofting laminate. Upon adding the same amount of fumaric acid as used for grafting to the control experiment containing virgin PPE, a laminate was obtained with one epoxy phase T_g and one plasticized PPE T_g at 124°C and 185°C, respectively. It delaminated after the solvent test.

PPE With (*Di-n-Butylamino*)Methyl Group on the Backbone

PPE with the (*di-n-butylamino*)methyl group on the backbone was made by the procedure developed by White and Nye.⁴ The virgin PPE was first treated with *N*-bromosuccinimide (NBS) to convert a portion of the methyl substituent on the polymer chain to the bromomethyl group. The brominated PPE was then treated with *di-n-butylamine* in toluene to form the modified PPE 7. Based on the NMR integration approximately every ten repeating units of



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the modified PPE contained one unit having one (*di-n-butylamino*)methyl substituent on the aro-

matic ring. Since the modified PPE had over ten thousand parts per million nitrogen on its backbone, the cocatalyst TMG might not be needed. Thus, a formulation without TMG was prepared using the amine-modified PPE. The cured laminate had no *Z*-axis expansion in the solder test. It suggested again the PPE/epoxy copolymer might have played a critical role in improving the lofting property of the laminate. Although it gained 16% of its original weight after the solvent test, the dried coupon after the solvent test did not lose any weight and had a smooth surface finish. It is evident that the formation of epoxy-grafted PPE initiated by the amine functionality on the PPE backbone hinders the dissolution of PPE in methylene chloride. However, the mechanism of solvent uptake is more involved and may be largely determined by the crosslinking density of the surface. Further, the PPE phase T_g of the laminate dropped to 164°C. It is difficult to assess how much the T_g drop can be attributed to the PPE/epoxy copolymer formation, since a well-defined T_g of the *di-n-butylamine*-modified PPE 7 could not be obtained by DSC. The material was slowly losing weight during the scan. At 300°C it lost almost 10% of its original weight (Fig. 1). The

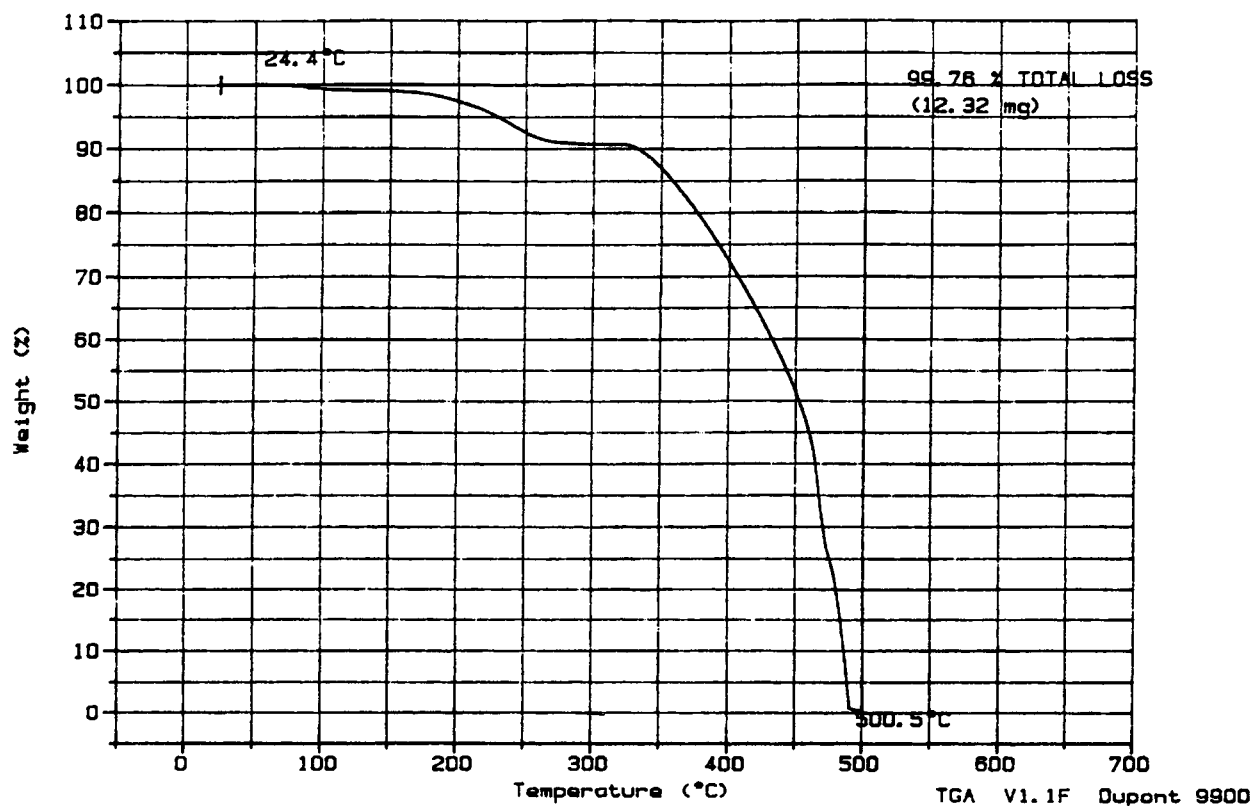


Figure 1 TGA of *di-n-butylamino*-modified PPE 7.

mechanism of the decomposition is not well understood. An attempt was made to analyze the final structure after the amine-modified PPE **7** had been heated at 300°C for 10 min. Unfortunately, the material became a crosslinked gel that was insoluble in any solvent.

Redistributed PPE

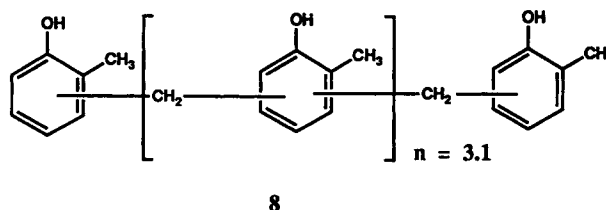
Redistribution With 3,3',5,5'-Tetramethyldiphenylquinone (TMDQ) and 4,4'-Isopropylidene-diphenol (BPA)

By carrying out the redistribution reaction of PPE¹⁰ with a radical initiator TMDQ and a diol, for example BPA, the concentration of the non-Mannich phenolic end groups increased significantly (Table I). The redistributed PPE also gave a system with better resin flow during lamination because of its lower molecular weight, although the foreseeable disadvantage of using redistributed PPE might be the lowering of PPE phase T_g . A treater run was carried out with the redistributed PPE obtained by equilibrating 0.46 i.v. PPE with 1% TMDQ (by weight, based on PPE) and 1% BPA (by weight, based on PPE) in toluene. The hydroxy content of the non-Mannich phenolic end group was raised from 0.089% in the virgin PPE to 0.237% in the redistributed PPE, and the T_g of the redistributed PPE was reduced to 211°C. The resulting laminate did not loft in solder test. Surprisingly, it had a PPE phase T_g at 212°C that is not very different from that of the PPE powder from which it was made. A detailed discussion of this phenomenon was published.¹¹ In the methylene chloride test the tested coupon had 3.5% weight gain, and showed only 0.26% weight loss after it had been dried in the heated vacuum oven overnight.

Redistribution With TMDQ and HT-9490

Redistributing PPE with TMDQ (1 wt % based on PPE) and a novolac resin HT-9490 **8** (1 wt % based on PPE) could generate a PPE with more reactive phenolic functionality per PPE molecule. The re-

sulting PPE should have even higher probability of forming PPE/epoxy copolymer during lamination. It had a hydroxy content of 0.240% (Table I), but the improvement of the laminate property was not significant. The laminate obtained from the PPE prepared from this approach had similar solvent resistance and solder expansion properties as the one made from TMDQ/BPA redistributed PPE, having a PPE phase T_g of 213°C.



Redistribution Attempts With Benzoyl Peroxide and Phenols Carrying Carboxylic Acid Functionality

Because both fumaric acid-grafted PPE and redistributed low molecular weight PPE gave nonlofting laminates, it would be interesting to find out if any processing advantage could be gained by using a low molecular weight PPE that also carries the carboxylic acid functionality. Some attempts were made to prepare the low i.v. carboxylic acid-functionalized PPE by the redistribution method. The molecular weight of 0.40 i.v. PPE was reduced after the PPE was treated with 2% of benzoyl peroxide (BPO) and 2% of one of the three hydroxybenzoic acid isomers. Although the three isomers have very different solubility in toluene, surprisingly, the PPEs resulting from the three redistribution reactions had almost identical molecular weight distributions. We could not identify any significant carboxylic acid functionality in any of them by FTIR. Further, a redistribution with only 2% BPO yielded a PPE having a similar molecular weight distribution as those derived from the redistribution with BPO and hydroxybenzoic acid isomers. It was clear that the three isomers of hydroxybenzoic acid were not incorpo-

Table I Analytical Data of Several PPE's Used in Preparation of PPE/epoxy Laminate

PPE	M_n (g/mol)	M_w (g/mol)	i.v. (dL/g)	OH (%)	T_g (°C)	Laminate PPE T_g (°C)
Virgin	23186	64645	0.445	0.089	218.0	187, 223
TMDQ/BPA treated PPE	12299	38060	0.363	0.237	210.6	212
TMDQ/HT9490 treated PPE	12475	35209	0.350	0.240	205.3	213

rated into PPE chain under the conventional PPE redistribution conditions. To make sure the lack of incorporation in the PPE redistribution reaction was not caused by the acidity of the hydroxybenzoic acid, the methyl esters of the three hydroxybenzoic acid isomers were also examined in the redistribution. Again, they were inert in the redistribution reaction. It is conceivable that the electron withdrawing group impedes the reactivity of the phenolic group by decreasing its nucleophilicity or raising its oxidation potential.¹⁰

Vacuum-Vented PPE Extrudate

It is also known that PPE's Mannich-type end group can be converted to the non-Mannich phenolic end by passing the PPE powder through a vacuum-vented extruder.⁴⁻⁶ Thus, the PPE hydroxy content derived from the non-Mannich end phenolic group was increased to 0.15% after extrusion (Table II). The extruded PPE pellets also have a higher molecular weight and T_g (219°C) than the virgin PPE. When the pellets were used in the same PPE/epoxy formulation, the resulting laminate again passed the solder test, showing no *Z*-axis expansion. It gained 4.5% of its original weight after the solvent test that is slightly better than the laminate obtained by using the fumaric acid-grafted PPE. The tested coupon did not lose any weight after being dried overnight. The laminate had a low PPE phase T_g at 203°C that might be attributed to the plasticization by the epoxy component.

Redistributing the vacuum-vented PPE extrudate with 1% BPA and 1% TMDQ produced a low i.v. PPE with 0.35% hydroxy content of the non-Mannich phenolic end groups, which is 50% more than that derived from the virgin PPE powder with the same procedure (Table II). With more reactive functional groups the PPE should deliver the best solder and solvent properties in the laminate. Indeed, the laminate made from it had no *Z*-axis ex-

pansion and the best solvent resistance among all the formulations tested. The laminate gained only 1.75% of its weight after the methylene chloride test, and showed no weight change after drying the tested coupon for 24 h in a heated vacuum oven. The laminate had a PPE phase T_g of 204°C, which was rather close to the T_g of the redistributed PPE (206°C) from which it was made.

The PPE obtained by redistributing vacuum-vented PPE extrudate with HT-9490 also yielded a laminate with excellent properties. The laminate still maintained the nonlofting property; however, it gained 4.3% of its original weight after solvent test and showed no loss of weight after drying.

Epoxy Variations

The laminates containing virgin PPE were not improved by replacing Epon 828 in the formulation with a 2 : 1 mixture of Epon 828 and Epon 1138 **9**. They had 8.8% expansion in the solder test and lost 2.4% of their original weight to methylene chloride. By comparison, the extruded PPE in the same formulation generated a nonlofting laminate with 218.1°C PPE phase T_g . It gained 5.2% of its original weight after the solvent test and did not lose any of its original weight to the solvent after drying overnight. It demonstrated that varying the epoxy components might not have any significant effect on the solder property of the cured laminate.

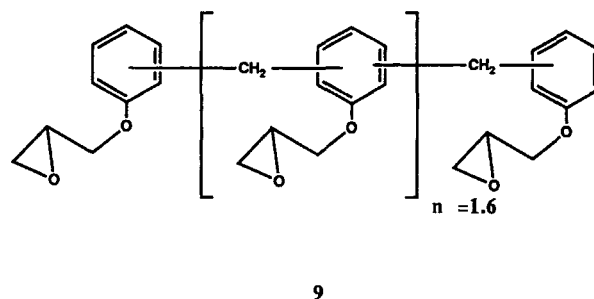


Table II Analytical Data of Several PPEs Used in Preparation of PPE/Epoxy Laminate

PPE	M_n (g/mol)	M_w (g/mol)	i.v. (dL/g)	OH (%)	T_g (°C)	Laminate PPE T_g (°C)
Virgin	23186	64645	0.445	0.089	218.0	187, 223
PPE extrudate	34260	82719	0.550	0.152	219.0	203
TMDQ/BPA treated extrudate	11651	49412	0.362	0.350	205.6	204
TMDQ/HT9490 treated extrudate	12208	52940	0.370	0.359	207.5	213

Table III Percentage of Crosslinked PPE After Compression Molding With Potential Crosslinkers

Compound	% of Crosslinked Material
	0
	10
	<3
	40
	60
	100
	90
	0
	27
	50

PPE Modifiers

Besides modifying PPE we were also interested in examining some reagents that would crosslink PPE at the curing temperature. With the PPE crosslinking reagent and the epoxy curing catalyst in the same formulation, an interpenetrating network of PPE and epoxy might be formed during lamination. Some acrylates¹² and quinone derivatives were tested as the potential crosslinkers for PPE. The screening was conducted by compression molding the PPE powder containing 10% of the potential crosslinker (by weight, based on PPE) at 270°C for 1 min. The molded film was then stirred in chloroform to remove the unreacted PPE. Finally, the crosslinked PPE was filtered, dried, and weighed. The percentage of the crosslinked PPE formed along with the reagents tested are listed in Table III. Interestingly, both the *ortho* and *para* isomers of chloranil stand out among all the compounds tested, giving close to quantitative yield of crosslinked PPE.

Benzoyl peroxide, *t*-butyl perbenzoate, and methyl ethyl ketone peroxide were also examined to determine their efficiency in crosslinking PPE in solid state. A toluene solution containing PPE and a peroxide (1, 3, 5, and 10 wt % based on PPE) was cast on a glass slide. The film was dried in a vacuum oven at room temperature before it was placed in a convection oven at 240°C for 50 min. The slide was then submerged in chloroform to examine the film's integrity. Interestingly all the PPE film became insoluble in chloroform after the tests. However, the less reactive peroxides, such as dialkyl peroxide and alkyl hydroperoxide may be more suitable for the study of the laminate formation because in the treating step the resin-coated glass cloth has to go through a heated oven (> 140°C) that removes the volatiles. Benzoyl peroxide, with a relatively short lifetime, may lose its reactivity completely in this drying process.

Table IV Properties of PPE/Epoxy Laminates Containing PPE Crosslinking Agents

Crosslinking Agent	Loading (%, based on PPE)	Solvent Resistance (%)	Z-Axis Expansion (%)	DMA T_g (°C)
<i>t</i> -Butyl peroxybenzoate	2.0	7.5, -2.0	15.0	201
<i>t</i> -Butyl peroxybenzoate	6.0	5.5, -1.7	11.4	138, 209
Methyl ethyl ketone peroxide	3.6	4.2, -0.5	7.1	132, 213
2,5-Dimethyl-2,5-di-(<i>t</i> -butylperoxy)-hexane	6.0	9.4, -1.0	0.2	160, 197
Cumene hydroperoxide	6.0	8.3, -1.3	7.5	206
Chloranil	6.0	14.0, -0.4	22.4	84, 199

The conventional formulation with 70/30 PPE/Epon 828 and Al(acac)₃ was used to test the PPE crosslinkers of choice. The laminate properties with the PPE crosslinking agents used are listed in Table IV. Unfortunately all except one of the laminates made with added PPE crosslinking agents, quinone derivatives as well as peroxides, lofted in the Z-axis expansion test (Table IV). Solvent resistance was not good for any of them either, as shown by the weight change after the test (first value in Table IV) and after oven drying (second value in Table IV).

CONCLUSIONS

PPE having carboxylic acid or a (*di-n*-butylamino)methyl group on the polymer chain facilitates the PPE-epoxy copolymer formation in the PPE/epoxy laminate. It was demonstrated that high copolymer content is essential in obtaining a non-lofting PPE/epoxy laminate. Using redistributed PPE and vacuum-vented PPE extrudate were also found to be useful in improving the solder property of the PPE/epoxy laminate. Further, the laminate with the best solvent resistance and solder expansion was obtained by using PPE that had been extruded first and then redistributed with BPA. Several acrylates, quinone derivatives, and peroxides were examined for their efficiency in crosslinking PPE. Incorporation of the PPE crosslinker and epoxy catalysts in the same formulation did not yield any laminates meeting the printed circuit board specifications.

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