Poly(2,6-dimethyl-1,4-phenylene ether) (PPO®) Capping and Its Significance in the Preparation of PPO®/Epoxy Laminate

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SYNOPSIS

The thermal expansion property at 288°C of poly(2,6-dimethyl-1,4-phenylene ether) (PPO®)/epoxy laminate was found to be affected by the PPO/epoxy copolymer content in the laminate. Capping of redistributed PPO with epoxide-containing reagents such as Araldite® EPN 1138 and an "upstaged" resin was readily accomplished with tetraethylammonium hydroxide or N,N-dimethylaminopyridine as the catalyst during the varnish preparation step. The resulting PPO/epoxy laminate maintained the nonlofting property despite the presence of phenolic hardener (curing accelerator) and antimony pentoxide (flame retardant) in the formulation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

High molecular weight poly(2,6-dimethyl-1,4-phenylene ether) (PPO®) resin was found to be miscible with 4,4'-isopropylidenediphenol diglycidyl ether (BPADGE) or Shell EPON® 828 at elevated temperature. The resulting mixture could be cured with added curing catalysts. Preliminary results indicated that the cured PPO/epoxy blends had excellent physical, chemical, and electrical properties. This intriguing combination of properties suggested application as a matrix material for circuit board[1]:

EPON® 828
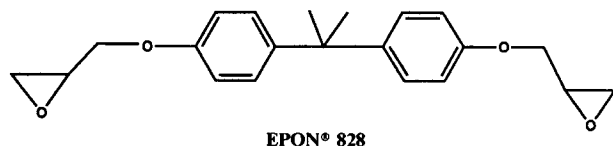
We demonstrated previously that by placing epoxy-reacting functionalities on PPO improved the properties of the resulting PPO/epoxy laminates, especially the thermal expansion property at 288°C.[2,3] However, the curing time for those laminates was considered to be too long to be practical.

After making several changes in the formulation, such as incorporating the phenolic hardener CK 210, increasing the weight ratio of the epoxy components, and employing a different catalyst package, the curing speed was improved. The new formulation yielded laminates of excellent thermal expansion property with the regular PPO of 0.40 or 0.46 intrinsic viscosity (i.v.). Unfortunately, by using the low i.v. PPO, prepared by a redistribution reaction[2] on the regular PPO, the new formulation no longer generated a laminate with acceptable thermal expansion property. This report detailed the approaches that we took to resolve the issue.

EXPERIMENTAL

General

All commercially available compounds were used as received without further purification. EPON 828 (bisphenol A diglycidyl ether) was purchased from Shell Chemical Co. PPO was obtained from Noryl® Products Section with an intrinsic viscosity (i.v.) of 0.46 or 0.40 dL/g. Araldite® EPN 1138, an epoxy phenol novolac resin, was purchased from Ciba-Geigy. CK 2103 was obtained from Union Carbide Corp. Lica® 12 was purchased from Kenrich Petroleum Chemicals, NJ. Zinc stearate was purchased

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from Alfa Products, Morton Thiokol Inc. Zinc octoate (Therm-Check® 705) was obtained from Bedford Chemical Division, Ferro Corp. Epolite® 2347 was purchased from Hexcel. It contains 1,2-dimethylimidazole (26%), N-methylpyrrolidone (47%), and m-phenylenediamine (27%). Ethacure®-100, a mixture of **1** and **2** in a ratio of 4 to 1 was obtained from Ethyl Corp. C17Z; an imidazole derivative was obtained from Shikoku Chemical Co. EFR-6 and ADP-480 were purchased from Nyacol Products Inc. Woven glass cloth (Burlington, #7628, 0.13125 g/in.²) was obtained from Electromaterial Division, Coshocton, OH. The "upstaged" epoxy solution 13359 was developed by J. Hallgren and V. Eddy. It was made by heating a mixture of 50 parts by weight of EPON 828, 30 parts of 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, 20 parts of EPN 1138, and 0.2 part of triphenylphosphine at 165°C for 1 h in a nitrogen atmosphere with stirring. All the glass transition temperature (T_g) data of the laminates were obtained via dynamic mechanical analysis (DMA). The DMA samples were run on a Rheometrics RSA-II solids analyzer equipped with an IBM PS/2 controller and a 3-point bend beam sample holder. This tool required a 12.7 × 52 mm sample. The samples were heated at 10°C/min using at 1 Hz frequency (6.28 radians/s) under a static air atmosphere. The applied strain was kept low to prevent sample buckling, 0.02%, and a small amount of auto tension was applied to maintain a constant force on the sample. The samples were heated from 50 to 260°C and a plot of E', E'', and tan delta was obtained. The T_g's of the epoxy fraction and the PPO fraction were calculated from the tan delta curve. GC analysis was performed on an HP5890 gas chromatograph using a Supelco SPB-1 (30 m, 0.32 mm i.d.) column with a Shimadzu C-R3A integrator:

EPN 1138

CK2103

1   **2**
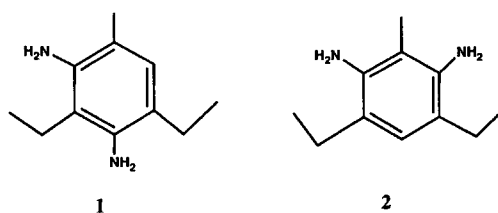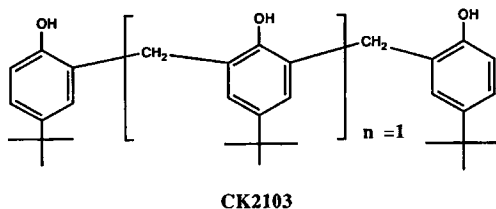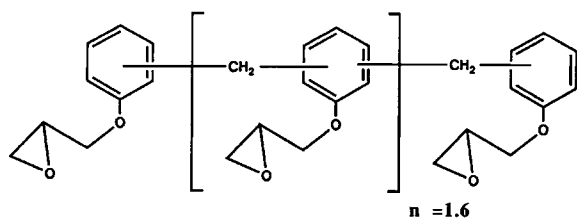
Preparation of Acetyl-capped PPO

Vacuum-vented PPO extrudate (300.0 g) was dissolved in 1200 mL of toluene at 90°C to form a homogeneous solution. To the solution were added acetic anhydride (30.0 g) and pyridine (60.0 g). Then, the solution was heated at reflux for 4 h. After the reaction was cooled to room temperature, methanol was added to the flask to precipitate the acetyl-capped PPO. The polymer was collected by filtration.

Preparation of Aryl-capped PPO

Vacuum-vented PPO extrudate (140.0 g) was dissolved in a mixture of N-methylpyrrolidone (400 mL) and toluene (200 mL) at 90°C under nitrogen. After the solution was brought to reflux (160°C), the finely ground anhydrous potassium carbonate (14.0 g) was added to it. For 2 h at reflux, water was removed azeotropically to ensure that the solution was anhydrous. 4-Fluorobenzophenone (20.0 g) was then added to the reaction, and the solution was kept at reflux overnight. After cooling, the reaction was diluted with 700 mL of chloroform before the polymer was precipitated with methanol. The filtered polymer was stirred in boiling water for 1 h to remove the salt. The aryl-capped PPO was filtered and dried overnight.

Preparation of Resin Solution (Varnish) with Acetyl- and Aryl-capped PPO (Runs 1 and 2)

To a 5 L three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer were added toluene (1400 mL) and modified PPO (500.0 g). The flask was heated to 90°C until a homogeneous solution was formed. To the solution were added EPN 1138 (66.7 g, 75% in toluene), "upstaged" resin 13359 (533.0 g, 75% solution), CK 2103 (100.0 g), zinc stearate or zinc(acac)₂ (20.0 g), Lica 12 (5.0 g), and Epolite (7.0 g) or C17Z (17.0 g) sequentially. After stirring for another 15 min, the solution was transferred to a 1 gal jug to be used in the treater immediately.

Preparation of Resin Solution (Varnish) with Redistributed PPO (Run 3)

To a 5 L three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer were added toluene (1400 mL), PPO (0.40 dL/g intrinsic viscosity, 500.0 g) and 4,4'-isopropylidenediphenol (BPA, 10.0 g). The flask was heated to 90°C until a homogeneous solution was formed. To the solution, 3,3',5,5'-tetramethyldiphenoquinone (TMDQ, 10.0 g) was added to initiate the PPO redistribution. After 2 h at 90°C, to the flask containing the redistributed PPO were added EPN 1138 (133.0 g, 75% in toluene), "upstaged" resin (533.0 g, 75% solution), CK 2103 (100.0 g), zinc stearate (30.0 g), Lica 12 (5.0 g), and Epolite (14.0 g) sequentially. After stirring for another 15 min, the solution was transferred to a 1 gal jug to be used in the treater immediately.

Model Reaction of Mesitol and Phenylglycidyl Ether Catalyzed by Tetraethylammonium Hydroxide (TEAH)

Mesitol (6.81 g, 0.05 mol), phenylglycidyl ether (7.51 g, 0.05 mol), and TEAH (5.89 g, 20% in aqueous solution) in toluene (150 mL) were heated at reflux, and the water was removed azeotropically. In 2 h, the adduct 3 was formed in 80% yield by GC analysis.

Model Reaction of Mesitol and Phenylglycidyl Ether Catalyzed by N,N-Dimethylaminopyridine (DMAP)

Mesitol (6.81 g, 0.05 mol), phenylglycidyl ether (7.51 g, 0.05 mol), and DMAP (0.5 g) in toluene (150 mL) were heated at reflux. In 1 h, the adduct 3 was formed in quantitative yield by GC analysis.

Model Reaction of 1-Phenyl-2-Propanol and Phenylglycidyl Ether Catalyzed by DMAP

1-Phenyl-2-propanol (6.81 g, 0.05 mol), phenylglycidyl ether (7.51 g, 0.05 mol), and DMAP (0.5 g) in toluene (150 mL) were heated at reflux for 1 h. Adduct 4 was formed in less than 5% yield by GC analysis.

Preparation of Resin Solution (Varnish) with Capped PPO of Low Molecular Weight

TEAH Catalyst (Run 4)

To a 5 L three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer were added toluene (1400 mL), PPO of 0.40 i.v. (500.0 g), and BPA (10.0 g). The flask was heated to 90°C until a homogeneous solution was formed. To the solution, TMDQ (10.0 g) was added to initiate the PPO redistribution. After 2 h at 90°C, to the flask containing the redistributed PPO were added EPN 1138 (133.0 g, 75% in toluene) and TEAH (3.75 g, 20% aqueous solution). The capping was conducted in reflux toluene, and water was removed azeotropically. After 2 h at reflux, the solution was cooled to 90°C and "upstaged" resin (533.0 g, 75% solution), CK 2103 (100.0 g), zinc stearate (30.0 g), Lica 12 (5.0 g), and Epolite (14.0 g) were then added sequentially. After stirring for another 15 min, the solution was transferred to a 1 gal jug to be used in the treater immediately.

DMAP catalyst (Run 11)

To a 5 L three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer were added toluene (1400 mL), PPO of 0.40 i.v. (500.0 g), and BPA (10.0 g). The flask was heated to 90°C until a homogeneous solution was formed. To the solution, TMDQ (10.0 g) was added to initiate the PPO redistribution. After 2 h at 90°C, to the flask containing the redistributed PPO were added EPN 1138 (67.0 g, 75% in toluene), "upstaged" resin (533.0 g, 75% solution), and DMAP (0.5 g). The capping was conducted in reflux toluene for 2 h. The solution was cooled to 90°C, and CK 2103 (100.0 g), zinc stearate (30.0 g), Lica 12 (5.0 g), and Epolite (14.0 g) were then added sequentially to it. After stirring for another 15 min, the solution was transferred to a 1 gal jug to be used in the treater immediately.

Preparation of Resin Solution (Varnish) Containing EFR-6 and Capped PPO of Low Molecular Weight (Run 14)

To a 5 L three-necked flask equipped with a mechanical stirrer, a condenser, and a thermometer were added toluene (1400 mL), PPO of 0.46 i.v. (600.0 g), and BPA (6.0 g). The flask was heated to 90°C until a homogeneous solution was formed. To the solution, benzoyl peroxide (6.0 g) was added to initiate the PPO redistribution. After 2 h at 90°C, to the flask containing the redistributed PPO were added EPN 1138 (120.0 g), "upstaged" resin (800.0 g, 75% solution), and DMAP (1.2 g). The capping was conducted in reflux toluene for 2 h. The solution was cooled to 90°C, and CK 2103 (120.0 g), zinc stearate (72.0 g), Lica 12 (6.0 g), EFR-6 (60.0 g),

Ethacure (11.55 g), and 1,2-dimethylimidazole (4.95 g) were then added sequentially to it. After stirring for another 15 min, the solution was transferred to a 1 gal jug to be used in the treater immediately.

Prepreg Formation

The resin solution was placed in a heated dip tank with no circulation. The 12 in. glass cloth passed through the dip tank in a preset speed to carry a 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 was determined by the cloth speed, the dip tank temperature, and the solid content of the solution. Usually, 40–44% resin content in the prepreg was considered acceptable.

Preparation of Laminates

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

Z-Axis Expansion

A strip of laminate (1 × 2 in.) was immersed in a solder bath at 288°C for 30 s. The sample was taken out of the bath and cooled, and the excess solder on the tested sample was scraped off. The difference in thickness before and after the test was measured with a caliper and recorded as the percentage of the original thickness. A nonlofting sample usually maintained its translucency before and after the test. A expanded sample often turned opaque after the solder test.

Solvent Resistance

A piece of laminate (2 × 2 in.) was soaked in methylene chloride for 30 min. It was then dried in the air for 10 min. The weight difference before and after the test was recorded as the percentage of the original weight. The result is listed as the first number under Solvent in the Appendix. The sample was 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 was recorded as the percentage of the original weight. The result is listed as the second number under Solvent in the Appendix.

RESULTS AND DISCUSSION

The main advantage of using the low i.v. PPO in the formulation was to improve the resin flow property during lamination. Also, the resulting prepreg was not as dusty as the one made from the regular PPO. Since the PPO/epoxy copolymer formation appeared to be the key in determining the laminate's thermal expansion property, it was conceivable the low i.v. PPO in the new formulation did not completely react with the epoxy before the epoxy phase became immobilized. Thus, to circumvent the insufficient copolymer formation issue, two approaches were taken: (1) capping PPO with epoxy components before final curing, and (2) using more epoxy in the formulation. The first approach might give PPO a head start in getting connected with the cured epoxy phase and the second increased the probability for PPO to react with epoxy resin.

To obtain a better understanding on the first approach, several end-capped PPO's (0.40 or 0.46 i.v.) were prepared and tested. The functional groups placed on PPO's end consisted of inert groups such as acetyl and aryl as controls and epoxides. The results from the acetyl- or aryl-capped PPO should determine whether the PPO/epoxy copolymer was crucial in forming good laminates. On the other hand, the PPO with one epoxide or two epoxides attached to the phenolic end groups should have different rates in forming the PPO/epoxy copolymer. The formulations of all the treater runs and the properties of the laminates resulting from them are attached in the Appendix.

Acetyl and Phenyl Capping

Acetyl Capping

The acetyl-capped PPO was made by reacting vacuum-vented PPO extrudate with acetic anhydride and pyridine. No residual hydroxyl group could be detected on the resulting PPO by FTIR. Replacing 0.40 i.v. PPO with the acetyl-capped PPO in a formulation known to give nonlofting laminates only produced laminates with serious lofting and poor solvent resistance (Run 1).

Aryl Capping

The acetyl group on the PPO end may be removed by the base catalyst or the hydroxyl group from the

epoxy curing. For this reason, an aryl-capped PPO was made by reacting vacuum-vented PPO extrudate with 4-fluorobenzophenone in N-methylpyrrolidone (NMP) with finely ground potassium carbonate as the base. The isolated material showed no residual hydroxyl absorption by FTIR. Moreover, the aryl group on the PPO end was expected to stay intact under the lamination conditions. Using the aryl-capped PPO in the control formulation again yielded a lofting laminate with poor solvent resistance (Run 2). It was clear that a nonlofting PPO/epoxy laminate could not be obtained with the capped PPO which cannot react with epoxy to form a copolymer.

Capping of Low i.v. PPO with Epoxy

Tetraethylammonium hydroxide (TEAH) has been a typical catalyst[4] used in catalyzing the reaction of phenol with epoxide in toluene, and under the reaction condition, TEAH usually does not induce too much epoxy–epoxy reaction. The TEAH-catalyzed reaction of mesitol, the model compound for one of the PPO phenolic end groups, and phenyl glycidyl ether, the model compound for epoxy components, in toluene was monitored by gas chromatography. After 2 h at reflux with continuous removal of water, 80% of the starting materials were consumed to form the adduct **3**. The catalyst TEAH may not be the ideal catalyst, but it certainly should promote the PPO capping to a certain extent. Indeed, capping low i.v. PPO with EPN 1138 at first helped a great deal prevent a fast-cure formulation from generating lofting laminates (Runs 3 vs. 4). To demonstrate that the benefit was not due to the extra TEAH added in the formulation, a treater run with the same amount of TEAH was conducted without the capping procedure (Run 5). The resulting laminate's solder property was not improved. Also, by comparing Run 4 with a similar run without CK 2103 in it (Run 6), it becomes evident that the solvent resistance property, i.e., crosslinking density, is improved greatly with the hardener under the same curing time. Nonetheless, both runs did not suggest any great differences between their laminates' solder property. When the level of CK 2103 in Run 4 was reduced by 50% (Run 7) and 75% (Run 8), laminates with excellent solder property were still formed with the extra capping step. The solvent property, however, fell in between Runs 4 and 6 as anticipated. We also realized as soon as CK 2103 was dropped to 50% of the level used in Run 4 the capping procedure was not essential any more in obtaining a nonlofting laminate (Run 9). However, the TEAH-catalyzed capping process (Run 7) seemed to in-

crease the curing rate slightly, which was manifested in the improvement of the laminate's solvent property at each curing time.

Since EPN 1138 is one of the high-priced components in the formulation, it would be desirable to use less of it. Based on Run 6, EPN 1138 was reduced by 50% to result in a 1–2 ratio of EPN 1138 to CK 2103, respectively, in Run 10. Unfortunately, with or without intentional capping of PPO, all the laminates expanded in the solder shock (Z-axis expansion) test. It may be because the TEAH-catalyzed capping of PPO with EPN 1138 was not complete or because the CK 2103 accelerated the epoxy curing such that the copolymer formation was seriously impeded. To answer the question, a more efficient capping catalyst had to be developed. 4-Dimethyl-aminopyridine (DMAP) is known to be an excellent catalyst for alkylation, acylation, and epoxy curing,[5] however, it has never been tested specifically to catalyze the reaction between phenol and epoxide. The model reaction of mesitol and phenylglycidyl ether was carried out in reflux toluene in the presence of a small amount of DMAP. Adduct **3** was obtained with a quantitative yield in 1 h. Furthermore, DMAP catalyzed the reaction of 1-phenyl-2-propanol, the model compound for the product of epoxy/epoxy or phenol/epoxy reaction, and phenylglycidyl ether to form Adduct **4** in 5% yield. It suggested that the undesirable epoxy curing reaction should be tolerable during the capping process. By repeating the Run 10 formulation with DMAP as the capping catalyst and using both EPN 1138 and "upstaged" resin as the capping reagents, all the laminates obtained were nonlofting (Run 11):

3

4
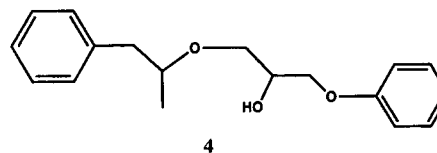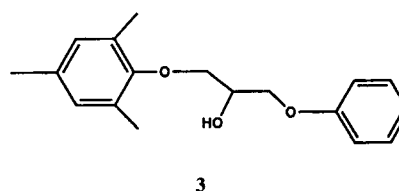
These experiments demonstrated that the ratio of hydroxyl to epoxy functionality in each formulation was crucial in determining the Z-axis expansion property of the PPO/epoxy laminate. By capping the PPO with epoxy components to ensure the

more rapid incorporation of PPO into the epoxy crosslinked matrix, the ratio of hydroxyl to epoxy groups could be increased without affecting the laminate's solder performance. Simultaneously, the curing rate was improved as evidenced by the laminate's T_g and solvent resistance.

More Epoxy Instead of Capping

When the ratio of CK 2103 to EPN 1138 was maintained at the same level as in Run 4, nonlofting laminates were obtained simply by raising the amount of the "upstaged" resin used in the formulation (Run 12). The PPO capping process was not needed. Obviously, the increased epoxide concentration from the extra "upstaged" resin helps produce enough PPO/epoxy copolymer during lamination.

PPO® Capping and Antimony Pentoxide

Antimony pentoxide was originally thought to be an inert ingredient in the epoxy formulation, acting as a synergist for the bromine-containing flame retardant. Thus, the research efforts on the PPO/ epoxy formulations had been concentrating on the antimony-free system. It was assumed that the antimony pentoxide could be added to any reasonable formulations to improve the laminate's flammability. Based on Run 13, a fast-cure formulation producing the laminates with all the desirable specifications except flammability, we started incorporating antimony pentoxide into the formulation. We tried EFR-6 (antimony pentoxide powder), modified ADP-480 (antimony pentoxide with Ethomeen T15 surfactant), calcium hydroxide-neutralized A 1550 (a 50% aqueous suspension of antimony pentoxide), and TEAH-neutralized A 1550. All the runs failed to generate nonlofting laminates. The repeated failures of an otherwise excellent formulation suggested that the antimony pentoxide was not an inert ingredient, at least in these formulations.

It was suspected that the antimony pentoxide might contain a fair amount of active hydroxyl groups, which could tip the desirable balance between the hydroxyl and epoxy concentrations upon which a nonlofting PPO/epoxy laminate was based. However, the situation might be corrected by precapping the PPO's phenolic end group with the epoxy components. In Run 14, the equilibrated PPO was first capped with the mixture of "upstaged" resin and EPN 1138 before adding EFR-6 and other ingredients. Indeed, the laminates derived from this run were all nonlofting. Further,

when the hardener CK 2103 was eliminated in the formulation, the capping procedure was not needed for the formulation to generate nonlofting laminates (Run 15).

CONCLUSIONS

The PPO/epoxy copolymer content in the PPO/ epoxy laminate was identified to be one of the crucial factors in determining the laminate's Z-axis expansion property. The efficiency of the copolymer formation is, in turn, established by the reactive functionalities and their concentrations on the PPO. However, the copolymer formation is also controlled by the accessibility of the epoxy components to the PPO's reactive functional groups during lamination. Hydroxyl-carrying ingredients such as phenolic hardener and the secondary alcohol in the "upstaged" resin may induce the epoxy phase to cure so fast that the resulting immobilized epoxy becomes inaccessible to the PPO phase during lamination. The issue was relieved by capping PPO with the epoxy components first to gain a head start in the PPO/epoxy copolymer formation, and the lofting problem in the laminate also disappeared. DMAP was found to be one of the best catalysts to catalyze the capping reaction in reflux toluene without inducing too much epoxy/epoxy reaction.

The flame-retardant antimony pentoxide was identified to be an active ingredient in the curing of the PPO/epoxy laminate. To incorporate antimony pentoxide in the formulation and still produce a nonlofting laminate, the original nonantimony formulation had to be modified by either eliminating the hardener CK 2103 or capping the PPO with the epoxy.

APPENDIX

Run 1

PPO, 500 g (extruded PPO capped with acetyl group, no detectable OH by FTIR); "upstaged" resin, 533.0 g (75%); EPN 1138, 67 g (75%); CK 2103, 100 g; C17 Z, 17.0 g; Zinc(acac)$_2$, 20 g; Lica 12 5.0 g.

Cure (min/°C)	Solder	DMA (°C)	Solvent
10/240	14.50%		0.5%; −1.7%

Run 2

PPO, 500 g (0.4 i.v., capped with 4-fluorobenzophenone); "upstaged" resin, 533.0 g (75%); CK 2103, 100.0 g; EPN 1138, 66.7 g (75%); Epolite, 7.0 g; zinc stearate, 20 g; Lica 12, 5.0 g.

Cure (min/°C)	Solder	DMA (°C)	Solvent
10/240	31.3%	116; 195.1	2.2%; −3.3%

Run 3

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g (75%); CK 2103, 100.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder
10/240	7.7%

Run 4

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ), tetraethylammonium hydroxide, 3.75 g (20%); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g; CK 2103, 100 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1/240	11.2% (blistered)		5.3%; 0.4%
2/240	0.0%	131.8; 185.5	6.0%; 0.8%
3/240	0.0%		3.9%; 0.3%
5/240	0.0%		2.5%; 0%
10/240	0.0%	140.6; 188.3	3.2%; 0.4%

Run 5

PPO, 500 g (0.4 i.v. equilibrated with 2% BPA and 2% TMDQ); tetraethylammonium hydroxide, 3.75 g (20%); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g; CK 2103, 100.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder
10/240	9.9%

Run 6

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ), tetraethylammonium hydroxide, 3.75 g (20%); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g (75%); CK 2103, 0.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1/240	3.7%		18.5%; −0.2%
2/240	0.0%	108.1; 164.6	14.1%; 3%
3/240	0.0%		10.1%; 2.8%
5/240	0.0%		8.5%; 2.3%
10/240	0.0%	128.8; 182.5	5.8%; 1.4%

Run 7

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ), tetraethylammonium hydroxide, 3.0 g (25%); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g (75%); CK 2103, 50.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1/240	0.0%		7.9%; 2.0%
1.5/240	0.7%		6.8%; 0.4%
2/240	0.0%		4.8%; 0.9%
3/240	0.0%		3.6%; 0.6%
5/240	0.0%		2.8%; 0.4%
10/240	0.0%	137.7; 194.2	2.3%; 0.2%

Run 8

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ), tetraethylammonium hydroxide, 3.0 g (25%); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g (75%); CK 2103, 25.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1/240	0.0%		7.9%; 2.0%
1.5/240	1.4%		11.1%; 1.5%
2/240	0.0%		5.3%; 1.2%
3/240	0.0%		6.0%; 1.4%
5/240	0.0%	125.6; 185.3	4.5%; 0.9%
10/240	0.0%		3.2%; 0.5%

Run 9

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ); EPN 1138, 133 g (75%); "upstaged" resin, 533.0 g (75%); CK 2103, 50.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent	Appearance After Solvent Test
1/240	2.3%	113.8; 176.5	10.3%; −0.48%	Blister
2/240	0.0%	125.7; 185.4	6.0%; 1.2%	Smooth surface
5/240	0.0%	136.7; 185.5	4.5%; 0.7%	Smooth surface
10/240	0.0%	137.7; 188.3	4.2%; 0.6%	Smooth surface

Run 10

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ); tetraethylammonium hydroxide, 3.75 g (20%); EPN 1138, 66.6 g (75%); (capping first); "upstaged" resin, 533.0 g (75%); CK 2103, 100.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	Comment
10/240	7.8%	Marginal laminate

Run 11

PPO, 500 g (0.4 i.v., equilibrated with 2% BPA and 2% TMDQ); EPN 1138, 67 g (75%); DMAP, 0.5 g; "upstaged" resin, 533.0 g (75%); (capping first); CK 2103, 100.0 g; Epolite, 14.0 g; zinc stearate, 30 g; Lica 12, 5.0 g; 2116 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1/240	0%	131.7; 189.3	7.3%; −0.1%
2/240	0%		5.2%; 0%
3/240	0%		6.3%; 0.7%
5/240	0%		6.0%; 0.5%
10/240	0%	134.8; 188.5	5.4%, 0.3%

Run 12

PPO, 600 g (0.46 i.v., equilibrated with 1% BPA and 1% BPO); EPN 1138, 160 g (75%); "upstaged" resin, 800.0 g (75% solution); CK 2103, 120 g; Epolite, 16.8 g; zinc stearate, 48 g; 7628 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1.5/240	0%	123.8; 201	1.67%; −1.1%
2/240	0%	127.7; 203	1.31%; 0%
5/240	0%	135.7; 203	1.51%; −0.2%

Run 13

PPO, 600 g (0.46 i.v., equilibrated with 1% BPA and 1% BPO), EPN 1138, 160 g (75%); "upstaged" resin, 800.0 g (75% solution); CK 2103, 120 g; Ethacure, 7.7 g; 1,2-dimethylimidazole, 3.3 g; zinc stearate, 48 g; Lica 12, 6.0 g; 7628 glass; 1950 mL toluene.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1.5/240	0.0%	127.7; 208.9	0.24%; −1.79%
5.0/240	0.0%	133.6; 212.9	0.64%; −0.64%
1.5/250	0.0%	131.7; 210.9	0.40%; −0.94%

Run 14

PPO, 600 g (0.46 i.v., equilibrated with 1% BPA and 1% BPO); EPN 1138, 120 g; "upstaged" resin, 800.0 g (75% solution); DMAP, 1.2 g (capping at 105°C for 2 h); CK 2103, 120 g; 11.55 g Ethacure + 4.95 g 1,2-dimethylimidazole; zinc stearate, 72 g; Lica 12, 6.0 g; EFR-6, 60 g; 7628 glass.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1.5/240	3.0%	104.3; 195.1	3.35%; −1.05%
3/240	0.0%		1.9%; −0.42%
5/240	0.0%	111.9; 203	2.15%; −0.1%
10/240	0.0%	112; 201.1	2.58%; 0%

Run 15

Flask 1: PPO, 600 g (0.46 i.v., equilibrated with 1% BPA and 1% BPO); toluene, 1500 mL; and Lica, 6.0 g. Flask 2: EPN 1138, 160 g (75% solution); "up-staged" resin, 800.0 g (75% solution); Solsperse, 4.8 g (30% solution); zinc octoate, 80 g; regular EFR-6, 48.0 g. After combining the contents of both flasks, add 11.52 g Ethacure, 5.04 g 1,2-dimethylimidazole, and 400 mL toluene to the mixture.

Cure (min/°C)	Solder	DMA (°C)	Solvent
1.5/240	0.0%	113.7; 193.2	3.01%; 0%
5/240	0.0%	121.8; 199.3	1.87%; 0.32%
10/240	0.0%	100.3; 195.3	1.82%; 0.44%

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