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(54) Title: VINYL-CAPPED POLY(PHENYLENE) ETHER AND STYRENE-BUTADIENE COPOLYMER BLENDS FOR CUR-
ABLE COMPOSITIONS

(57) Abstract: A composition comprising: a) a vinyl poly(phenylene) ether; b) a styrene-butadiene copolymer; c) optionally a vinyl-
benzyl ether of naphthol novolac; and d) a free radical initiator, a method for making the composition, and end uses for the composi-
tion are disclosed.



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VINYL-CAPPED POLY(PHENYLENE) ETHER AND STYRENE-BUTADIENE COPOLYMER BLENDS FOR CURABLE COMPOSITIONS

BACKGROUND OF THE INVENTION

5 Field of the Invention

Embodiments of the present disclosure relate to curable compositions and in particular to curable compositions that include polymers and a method of producing the curable compositions.

10 Introduction

Curable compositions are compositions that include thermosettable monomers that can be crosslinked. Crosslinking, also referred to as curing, converts the curable compositions into crosslinked polymers (ie., a cured product) useful in various fields such as, for example, composites, electrical laminates and coatings. Some properties of
15 curable compositions and crosslinked polymers that can be considered for particular applications include mechanical properties, thermal properties, electrical properties, optical properties, processing properties, among other physical properties.

For example, glass transition temperature, dielectric constant and dissipation factor can be properties that are considered to be highly relevant for curable compositions
20 used in electrical laminates. For example, having a sufficiently high glass transition temperature for an electrical laminate can be very important in allowing the electrical laminate to be effectively used in high temperature environments. Similarly, decreasing the dielectric constant and dissipation factor of the electrical laminate can assist in separating a current carrying area from other areas.

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To achieve desirable changes in glass transition temperature (T_g), dielectric constant (D_k) and dissipation factor (D_f), previous approaches have added various materials to curable compositions. Polybutadiene (PB) has been used to make low D_k/D_f

laminates due to its outstanding dielectric performance and a fully cured material has relatively good thermal resistance. However, PB based prepregs normally have issues with stickiness and the material is highly flammable. Also, the cured material has a T_g lower than 150°C, and it appeared as a wide T_g peak in a DMTA curve, which may be due to the resin was not fully cured. Styrene-butadiene copolymer (SBC) can be also be used for low D_k/D_f laminates. However, it can encounter similar issues. Vinyl capped polyphenylene ether (PPO) is also being developed for low D_k/D_f laminates. The cured PPO has high T_g and good flame retardant performance. However, the D_k and D_f of the cured product are not as good as those of butadiene based systems. Therefore, an affordable electrical laminate with desirable thermal properties and electrical properties would be beneficial.

SUMMARY

One broad aspect of the present invention comprises, consists of, or consists essentially of a) a vinyl poly(phenylene) ether; b) a styrene-butadiene copolymer; c) optionally a vinyl-benzyl ether of naphthol novolac and d) a free radical initiator.

DETAILED DESCRIPTION

The composition contains a vinyl poly(phenylene) ether (vinyl PPO). This resin contains one or more vinyl end groups. Examples of vinyl PPOs that can be used in the present invention include, but are not limited to SA9000SABIC PPO and OPE-2St MGC PPO.

The vinyl PPO is generally present in the range of from about 1 weight percent to 99 weight percent, is present in the range of from 25 weight percent to 75 weight percent in another embodiment and is present in the range of from 30 weight percent to 60 weight percent in yet another embodiment, based on the total weight of the composition.

The vinyl PPO generally has a number average molecular weight (M_n) in the range of from 300 to 25000, has a M_n in the range of from 800 to 10000 in another embodiment, and has a M_n in the range of from 1500 to 4000 in yet another embodiment.

The composition also contains styrene-butadiene copolymer. In an embodiment, the styrene-butadiene copolymer can contain over 50% 1,2-vinyl groups and in the range of from 17 to 27% styrene.

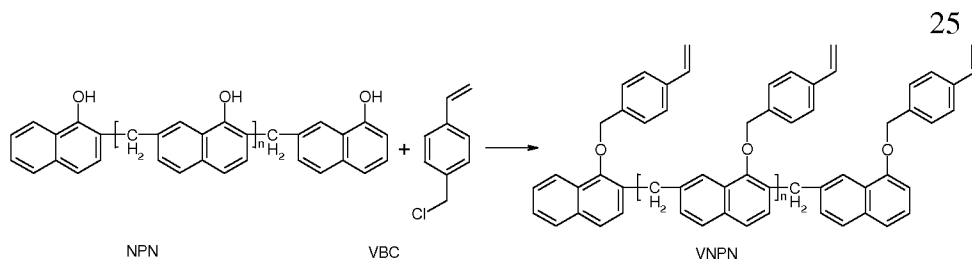
The styrene-butadiene copolymer is generally present in the range of from 40 weight percent to 75 weight percent and is present in the range of from 50 weight percent to 70 weight percent in another embodiment, based on the total weight of the composition. If the styrene-butadiene copolymer content is less than 40 weight percent, the Df will not improve significantly and if it is greater than 70 weight percent, it will induce low glass transition temperature (T_g).

The styrene-butadiene copolymer generally contains from 1 weight percent to 99 weight percent styrene, contains from 10 weight percent to 50 weight percent styrene in another embodiment, and contains 15 to 30 weight percent styrene in yet another embodiment.

The styrene-butadiene copolymer generally contains from 30 weight percent to 85 weight percent 1,2-vinyl groups and contains 50 to 70 weight percent 1,2-vinyl groups in another embodiment. If the 1,2-vinyl group content is less than 30 weight percent, it will induce low T_g or phase separation.

The styrene-butadiene copolymer generally has a number average molecular weight in the range of from 500 to 8000. If the molecular weight of styrene-butadiene copolymer is larger than 8000, it will induce phase separation.

In an embodiment, the composition also includes a vinyl benzyl ether of naphthol novolac (VNPN). The VNPN is optional. VNPN can be synthesized by reacting naphthol novolac (NPN) with vinyl benzyl chloride (VBC) as depicted below:



The vinyl-benzyl ether of naphthol novolac generally has a number average molecular weight of from 400 to 1500 and has a hydroxyl group content of less than 1 weight percent, based on the total weight of the vinyl-benzyl ether of naphthol novolac.

5 Vinyl benzyl ethers of naphthol novolac are generally present in the range of from about 0 weight percent to 99 weight percent, are present in the range of from 25 weight percent to 75 weight percent in another embodiment and are present in the range of from 30 weight percent to 60 weight percent in yet another embodiment, based on the total weight of the composition.

10

The composition also includes a free radical initiator to promote a free radical reaction. Examples of free radical initiators include but are not limited to dialkyldiazenes (AIBN), diaryl peroxides (BPO), dicumyl peroxide(DCP), cumene hydroperoxide (CHP), tert-butyl hydroperoxide (tBHP), and disulfides. Commercial
15 examples of free radical initiators that can be used in the present invention include, but are not limited to Luperox-F40P and Luperox-101 from Arkema Company.

Such initiators can be used alone and in combination to determine the onset initiating temperature of the free radical reaction. The free radical initiator is generally present in the range of from about 0.01 weight percent to 10 weight percent, is
20 present in the range of from 0.1 weight percent to 8 weight percent in another embodiment and is present in the range of from 2 weight percent to 5 weight percent in yet another embodiment, based on the total weight of the composition.

The composition can also contain a flame retardant. Examples of flame retardants that can be used include but are not limited to brominated or non-brominated resins,
25 brominated additives, non-brominated additives, and phosphorous based flame retardant agents.

The flame retardant is generally present in the range of from about 0 weight percent to 99 weight percent, is present in the range of from 0 weight percent to

70 weight percent in another embodiment and is present in the range of from 5 weight percent to 60 weight percent in yet another embodiment, based on the total weight of the composition.

5 Fillers can optionally be present in the composition. Examples include but are not limited to silica, talc, aluminum trihydrate (ATH), and magnesium hydroxide.

 Fillers can be generally present in the range of from about 0 weight percent to 80 weight percent, can be present in the range of from 1 weight percent to 50 weight percent in another embodiment and can be present in the range of from 1 weight percent to 30 weight percent in yet another embodiment, based on the total weight of the composition.

 The composition can also contain optionally one or more solvents. Examples of solvents include but are not limited to methyl ethyl ketone (MEK), dimethylformamide (DMF), ethyl alcohol (EtOH), propylene glycol methyl ether (PM), propylene glycol methyl ether acetate (DOWANOLTM PMA) and mixtures thereof.

 Solvents can be generally present in the range of from about 0 weight percent to 60 weight percent, can be present in the range of from 1 weight percent to 50 weight percent in another embodiment and can be present in the range of from 30 weight percent to 40 weight percent in yet another embodiment, based on the total weight of the composition.

 The composition can be prepared by any suitable method known by those skilled in the art. In an embodiment, a styrene-butadiene copolymer solution is admixed with a vinyl PPO solution. A flame retardant and initiator are also added, along with any other desired components, such as fillers. In an embodiment, a vinyl-benzyl ether of naphthol novolac is also added.

 In another embodiment of the present invention there is disclosed a method for preparing a prepreg comprising a) admixing the composition described above with a solvent to form a varnish; b) incorporating the varnish onto a substrate to form a

coated substrate; and c) drying the coated substrate at a drying temperature in the range of from 130°C to 160°C for an amount of time in the range of from 2 minutes to 6 minutes to form a prepreg.

The varnish can be incorporated onto the substrate by any suitable method.

- 5 Examples include but are not limited to rolling, dipping, spraying, brushing and/or combinations thereof. The substrate is typically a woven or nonwoven fiber mat containing, for instance, glass fibers or paper.

The coated substrate is "B-staged" by heating at a temperature sufficient to draw off solvent in the formulation and optionally to partially cure the formulation, so that the
10 coated substrate can be handled easily. The "B-staging" step is usually carried out at a temperature of from 90 °C to 210 °C and for a time of from 1 minute to 15 minutes. In an embodiment, the coated substrate is dried at a temperature in the range of from 130°C to 160°C and is dried for an amount of time in the range of from 2 minutes to 6 minutes.

The substrate that results from B-staging is called a "prepreg." One or more
15 sheets of prepreg are stacked or laid up in alternating layers with one or more sheets of a conductive material, such as copper foil, if an electrical laminate is desired.

The laid-up sheets are pressed at high temperature and pressure for a time sufficient to cure the resin and form a laminate. The temperature of this lamination step is usually between 100 °C and 230 °C, and is most often between 165 °C and 190 °C. The
20 lamination step may also be carried out in two or more stages, such as a first stage between 100 °C and 150 °C and a second stage at between 165 °C and 190 °C. The pressure is usually between 50 N/cm² and 500 N/cm². The lamination step is usually carried out for a time of from 1 minute to 200 minutes, and most often for 45 minutes to 90 minutes. The lamination step may optionally be carried out at higher temperatures for
25 shorter times (such as in continuous lamination processes) or for longer times at lower temperatures (such as in low energy press processes).

Optionally, the resulting laminate, for example, a copper-clad laminate, may be post-treated by heating for a time at high temperature and ambient pressure. The temperature of post-treatment is usually between 120 °C and 250 °C. The post-treatment
30 time usually is between 30 minutes and 12 hours.

EXAMPLES

The following materials were used in the Examples below:

Ricon[®] 100 resin (styrene butadiene random copolymer with about 70% 1,2 vinyl and 17-27% styrene) from Sartomer

5 Ricon[®] 181 resin (styrene butadiene random copolymer with about 30% 1,2 vinyl and 25-35% styrene, average Mn: 3000-3500) from Sartomer

Ricon[®] 184 resin (styrene butadiene random copolymer with about 30% 1,2 vinyl and 25-35% styrene, average Mn: 8000-9000) from Sartomer

10 SA9000 (Vinyl PPO, vinyl-capped Polyphenylene Ether Oligomer (Mn is about 1600)) from SABIC

Self-synthesized V-NPN synthesized with a number average molecular weight of 1045 and average hydroxyl value of 67

1,2-Bis(2,3,4,5,6-pentabromophenyl)ethane flame retardant from Unibrium Corp.

15 DCP (Dicumyl Peroxide), AIBN (dialkyldiazenes), BPO (diaroyl peroxides), TBHP (Tert-butyl hydroperoxide), CHP (Cumene Hydroperoxide) from Sinopharm Chemical Reagent Co. Ltd.

Preparation

20 Examples 1-24 and Comparative Example A

A free radical curing reaction between SBC and vinyl PPO (SA9000) was carried out as follows: SBC resin was dissolved in MEK to make a 50% SBC/MEK solution. Vinyl PPO resin was dissolved in MEK or Xylene or Toluene (according to different formulations) to make a 50% PPO/MEK solution. The two solutions were then mixed
25 together and were mixed with flame retardant 1,2-Bis(2,3,4,5,6-pentabromophenyl)ethane. Free radical initiators were added to make a homogeneous varnish. The resin formulation was hand-brushed onto 1080# glass fiber fabrics and the solvent was removed in a vacuum oven at different temperatures for various minutes

(according to different formulations). Samples were pressed with 8 ply and cured at 220°C for 2 hours and the properties of the casted samples were tested.

Treater run conditions:

5 Varnishes were prepared by the procedure as listed above. For the treater run, prepregs were dried at 145°C with the fabrics speed at 2m/min. Laminates were pressed with 6 ply of 2116# glass fabrics.

10 Examples 1-12 were prepared according to the following formulation: 22% Ricon 100[®], 22% SA 9000, 18% Bromine flame retardant, 1% DCP, and 37% MEK solvent. listed in Table 1 below and cured at 220°C for 2 hours. 1080# glass fabrics were used to make hand brushing boards. The properties of these compositions, with different drying times and temperatures, are shown in Table 1, below.

Comparative Example A and Examples 13-17 were prepared according to the formulations listed in Table 2 below and cured at 220°C for 2 hours. 1080# glass fabrics were used to make hand brushing boards.

15 Comparative Examples B and C and Examples 18-22 were prepared according to the formulations listed in Table 3 below and cured at 220°C for 2 hours. 1080# glass fabrics were used to make hand brushing boards.

Examples 23 and 24 were prepared according to the formulations listed in Table 4 below and cured at 220°C for 2 hours. 2116# glass fabrics were used to make treater run boards.

Table 1: Laminate properties with prepregs dried at different temperatures for different lengths of time

	Prepreg Drying T (°C)	Prepreg Drying Time (min)	Laminate Tg (°C)	Laminate Df	Laminate Dk
Example 1	120	3	170	0.003	2.95
Example 2	120	5	172	0.0029	2.93
Example 3	130	3	188	0.0027	3.02
Example 4	130	5	184	0.0026	3.05
Example 5	140	3	194	0.0028	2.9
Example 6	140	5	188	0.0019	2.88
Example 7	150	3	190	0.0023	3.09
Example 8	150	5	187	0.0021	2.97
Example 9	160	3	182	0.0021	2.88
Example 10	176	3	162	0.002	3.06
Example 11	176	5	160	0.002	2.95
Example 12	180	3	156	0.002	3.05

As is evident from the table above, the drying temperature is correlated with the Tg of the laminate. The most suitable drying temperature was in the range of from 130°C to 160°C (Examples 3-9), while temperatures lower than 130°C (Examples 1-2) or higher than 160°C (Examples 10-12) were correlated with reduced Tg of the laminates. A longer drying time can benefit Df, but may not benefit the Tg.

Table 2: Formulation, electrical properties and thermal performance of SBC/PPO laminate with different initiators

Components	Comparative Example A (solid wt/g)	Example 13 (solid wt/g)	Example 14 (solid wt/g)	Example 15 (solid wt/g)	Example 16 (solid wt/g)	Example 17 (solid wt/g)
SBC	10	10	10	10	10	10
Vinyl PPO	10	10	10	10	10	10
FR	8.28	8.28	8.28	8.28	8.28	8.28
BPO		0.4				
CHP			0.4			
BTHP				0.4		
AIBN					0.4	
DCP						0.4
Prepreg dried condition	150°C 3min	150°C 3min	150°C 3min	150°C 3min	150°C 3min	150°C 3min
Gel time/ s at 150°C	>10min	150	240	240	220	240
Resin content / %	78	76	75	76	75	75
Br content in resin / %	24	24	24	24	24	24
Bake condition	220°C 2h	220°C 2h	220°C 2h	220°C 2h	220°C 2h	220°C 2h
T _g / °C(DMA)	NA	152	135	134	185	190
Dk/1GHz	NA	2.69	2.92	2.84	3.56	3.63
Df/1GHz	NA	0.002	0.002	0.002	0.002	0.002

As is evident from the Table above, if an initiator was not added, then the gel time exceeded 10 minutes and the boards were not pressed successfully (Comparative

- 5 Example A). Low and medium-temperature initiators (AIBN in Example 16 and DCP in Example 17) had good initiating efficiency for the SBC/PPO system, but high temperature initiators (BPO in Example 13, CHP in Example 14, and BTHP in Example 15) did not work well in the SBC/PPO system, resulting in low T_g.

Table 3: Formulation, thermal performance, Tg, Dk, Df, FR performance and Cu-peel strength of SBC/PPO laminate

Components	Comp.Exam ple B (solid wt/g)	Comp. Example C (solid wt/g)	Example 18 (solid wt/g)	Example 19 (solid wt/g)	Example 20 (solid wt/g)	Example 21 (solid wt/g)	Example 22 (solid wt/g)
SBC	10 (Ricon 181)	10 (Ricon 184)	12(Rico n 100)	11(Rico n 100)	10(Rico n 100)	9(Ricon 100)	8(Ricon 100)
Vinyl PPO	10	10	8	9	10	11	12
FR	8.28	8.28	8.28	8.28	8.28	8.28	8.28
DCP	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Gel time / s(150C)	240	250	240	240	220	240	235
Resin content / %	76	75	76	75	75	75	75
Br content in resin / %	24	24	24	24	24	24	24
Prepreg drying temp. and time	150°C 3min	150°C 3min	150°C 3min	150°C 3min	150°C 3min	150°C 3min	150°C 3min
BakeCondition	220°C 2h	220°C 2h	220°C 2h	220°C 2h	220°C 2h	220°C 2h	220°C 2h
Tg / °C(DMA)	140	Phase separati on	170	183	190	196	195
Dk/1GHz	2.82	NA	2.76	2.91	2.96	2.85	2.75
Df/1GHz	0.002	NA	0.0024	0.0022	0.0025	0.0026	0.0027
Td / °C	350	NA	360	374	383	365	360
T288 / min	50	NA	>60	>90	>90	60	55
FR Performance (UL-90)	V-0	NA	V-0	V-0	V-0	V-0	V-0
Peel Strength / (lb / in)	6.7	NA	8.4	7.8	8.0	7.5	7.1

As is evident from the above Table, use of PPO resulted in high Tg, particularly at a high PPO to SBC ratio, although Df increased a little due to higher PPO content (Examples 19-22). When the Ricon 100 content was high (Example 18), the Tg decreased. Use of the Ricon 181 resin largely resulted in decreased Tg due to much lower vinyl bonds in the resin (Comparative Example B) and the Ricon 184 resin had a phase separation problem due to its large molecular weight (Comparative Example C). It is also evident that SBC/PPO laminates (with a SBC/PPO ratio of 6/4 to 4/6, Examples 20-24) show good thermal and flame retardant performance as well as good copper peel strength.

Table 4: Formulations for treater run and thermal properties, Tg, Dk, Df, FR performance and Cu-peel strength of laminate

Components	Example 23 (solid wt/g)	Example 24 (solid wt/g)
PPO/Solvent	1000g/ 352gToluene+600gMEK	1000g/352gToluene+600gMEK
Ricon 100/Solvent	1000g/ 935gMEK+(560gMEK+140gToluene)	1000g/935gMEK+(560gMEK+140gToluene)
FR	791g(23%)	791g(23%)
Filler/ SiO ₂	none	677g (20%)
Initiator/ DCP	40g	40g
Vinyl silane/ (0.5wt%@SiO ₂)	none	3.4g
Varnish solid content / %	60	60
Varnish Gel time / s (150C)	260	250
Prepreg gel time / s (150C)	100	100
Prepreg residual solvent/ %	0.2	0.18
Prepreg resin content / %	48%	54%
Prepreg drying temp. and time	145°C 4min	145°C 4min
Cure protocol:	220 2h	220 2h
Resin content / %	44	50
Br content in resin / %	23	23
Laminate thickness / mm	0.84	1.05
Laminate residual solvent/ %	0.2	0.22
Dk @ 1GHz	3.54	3.54
Df @ 1GHz	0.0024	0.0027

Tg (DMA) / °C	185	182
Td / °C	406	410
T288 / min	>90	>80
FR Performance (UL-90)	V-0 (<1s)	V-0 (<3s)
Peel Strength / (lb / in)	>8	>8
Interlayer adhesive strength /	NA	NA
Water absorption (wt.%)	0.17	0.15
Solder dip	Pass	Pass
Average CTE/ppm(z-axis, below Tg)	103	74
Toughness ranking	Good	Good

As is evident from the Table above, the average CTE of the laminate with fillers (Example 24) was improved compared with the laminate without fillers (Example 23), due to the movement restriction effect of polymer chains by fillers.

Examples 25-26 and Comparative Examples D-H

- 5 A free radical curing reaction between SBC and vinyl PPO (SA9000) was carried out as follows: SBC resin was dissolved in MEK to make a 50% SBC/MEK solution. Vinyl PPO resin was dissolved in MEK to make a 50% PPO/MEK solution. V-NPN was dissolved in MEK to make a 50% V-NPN/MEK solution. The three solutions were mixed together and mixed with a flame retardant 1,2-Bis(2,3,4,5,6-
- 10 pentabromophenyl)ethane. Free radical initiators were added to make a homogeneous varnish. The resin formulation was then hand-brushed onto 1080# glass fiber fabrics and solvent was removed in a vacuum oven at 150°C for 3 minutes. Samples were pressed with 8 layers and cured at 200°C for 3 hours and at 250°C for 1 hour and the properties of the casted samples were tested.
- 15 The following board pressing protocol was used: The temperature was increased to 150°C. Force was then exerted with 24000 pounds at 150°C. This was repeated several times in order to exhaust the bubbles. The temperature was then increased from 150°C to

200°C, and this temperature was kept constant for 3 hours. The temperature was then increased to 250°C, and this was kept constant for 1 hour, after which the temperature was decreased to room temperature.

- 5 Comparative Examples D-H and Examples 25-26 were prepared according to the formulations listed in Table 8 and cured at conditions listed in Table 5, below.

Table 5 Formulation, electrical properties and thermal performance of SBC/PPO/V-NPN laminates

Components	Comp Example D (solid wt/g)	Comp Example E (solid wt/g)	Comp Example F (solid wt/g)	Comp Example G (solid wt/g)	Comp Example H (solid wt/g)	Example 25 (solid wt/g)	Example 26 (solid wt/g)
SBC	10	0	0	10	8	8	10
Vinyl PPO	10	10	0	0	8	8	2
V-NPN		10	20	10	10	4	8
FR1	8.28	8.28	8.28	8.28	8.28	8.28	8.28
DCP	0.4	0.4	0.2	0.4	0.48	0.4	0.4
Gel time(150 °C)/s	220	200	200	240	240	240	260
Resin content / %	78	76	75	76	75	75	75
Br content in resin / %	24	24	24	24	24	24	24
Bake condition	200°C 3h+250°C 1h	200°C 3h+250°C 1h	200°C 3h+250°C 1h	200°C 3h+250°C 1h	200°C 3h+250°C 1h	200°C 3h+250°C 1h	200°C 3h+250°C 1h
Tg / °C(DMA)	190	Phase separation	240	Phase separation	205/239 (Two peaks)	212	237
Dk/1GHz	3.01	NA	3.21	NA	3.51	3.00	3.15
Df/1GHz	0.0025	NA	0.008	NA	0.0011	0.0029	0.0030
Td / °C	360	NA	383	NA	NA	362	370
T288 / min	>60	NA	>60	NA	NA	>60	>60
FR Performance (UL-90)	V-0	NA	V-0	NA	V-0	V-0	V-0

As is evident from the above table, the SBC/Vinyl PPO blends had a moderate Tg and low Dk and Df (Comparative Example D). Vinyl PPO/V-NPN blends (Comparative

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Example E) or SBC/V-NPN blends (Comparative Example G) had phase separation problems due to polarity differences between the components. Neat V-NPN (Comparative Example F) can be cured with an initiator and resulted in a high T_g, however, the D_f was also as high as 0.008 and the laminate was quite fragile. Through suitable composition adjustment for SBC/Vinyl PPO/V-NPN, the phase separation problem can be avoided and a laminate with high T_g and low D_k, D_f was obtained, as shown in Examples 25 and 26. However, if the SBC content was less than 30% of resin in the formulation, there were two T_g peaks shown in DMTA curve, indicating phase separation in the laminate (Comparative Example H). The laminates in Comparative Examples D, F and Examples 25 and 26 all had acceptable T_d and T₂₈₈, and also good flame retardant performance with 24% Br content.

Test Methods

Decomposition temperature (T_d) of the cured resins was performed by Thermogravimetry analysis (TGA) with Instrument TGA Q5000 V3.10 Build 258. The test temperature ranges from room temperature to 700 °C for all the examples and comparative examples; the heating rate is 20°C/min, nitrogen flow protection. The decomposition was determined through selecting the corresponding temperature at 5% of weight loss (residual weight 95%) of materials.

Glass transition temperature (T_g) of the cured resins was determined with RSA III dynamic mechanical thermal analyzer (DMTA). Samples were heated from -50 to 250°C at 3°C/min heating rate. Test frequency was 6.28 rad/s. The T_g of the cured resin was obtained from the tangent delta peak.

The dielectric constant and dissipation factor (D_k and D_f) were determined by ASTM D-150 employing an Agilent E4991A RF impedance/material analyzer under 1 GHz at room temperature. The sample thickness was 0.3~3.0 millimeters. To obtain a Tier 5 laminate, D_f value should be controlled under 0.005.

T288 was measured using a TA instrument TMA Q400 operating at a 10°C/min heating rate and isothermal at 288°C of an unclad sample of 6.4 mm x 6.4 mm. The failure (delamination) of the sample is evidenced by a sudden and rapid indication of expansion
5 in the plot of time vs. Z-dimension.

FR test: The varnish was brushed on 1080# or 2116# glass fabrics and baked in an oven for 3-5 min at various temperatures to obtain prepregs (according to different formulations). The prepreg sheets were molded into a laminate and cured by a regular
10 hot press machine. The final laminate was cut into the standard samples for UL-94 FR testing.

Gel time: The gel time is the amount of time necessary for a resin to meet its gel point (the point at which the resin turns from a viscous liquid to an elastomer). The gel time
15 was measured and recorded using approximately 0.7 ml of liquid dispensed on a hot plate maintained at 176°C, stroking the liquid back and forth after 60s on the hot-plate until it gelled.

CLAIMS

WHAT IS CLAIMED IS:

1. A composition comprising:
 - a) a vinyl poly(phenylene) ether ;
 - 5 b) a styrene-butadiene copolymer;
 - c) optionally a vinyl-benzyl ether of naphthol novolac; and
 - d) a free radical initiator.
2. A composition in accordance with claim 1 wherein the vinyl poly(phenylene) ether has a number average molecular weight in the range of from 300-
10 5000.
3. A composition in accordance with any one of claims 1 or 2 wherein the vinyl-benzyl ether of naphthol novolac has a number average molecular weight of from 400 to 1500 and has a hydroxyl group content of less than 1 weight percent, based on the total weight of the vinyl-benzyl ether of naphthol novolac.
- 15 4. A composition in accordance with any one of the preceding claims wherein the styrene-butadiene copolymer is present in an amount in the range of from 40 weight percent to 70 weight percent the vinyl(poly)phenyl ether is present in an amount in the range of from 25 weight percent to 75 weight percent, the vinyl-benzyl ether of naphthol novolac is present in an amount in the range of from 25 weight percent to 75
20 weight percent and the initiator is present in the range of from 0.01 weight percent to 10 weight percent, based on the total weight of the composition.
5. A composition in accordance with any one of the preceding claims wherein the styrene-butadiene copolymer has a number average molecular weight from 500 to 8000, has a styrene content in the range of from 10 weight percent to 50 weight
25 percent and a 1,2-vinyl group content in the range of from 30 weight percent to 85 weight percent, based on the total weight of the styrene-butadiene copolymer.
6. A composition in accordance with any one of the preceding claims further comprising:

e) a flame retardant.

7. A composition in accordance with any one of the preceding claims wherein said initiator is selected from the group consisting of dialkyldiazenes, diaryl
5 peroxides, dicumyl peroxide, tert-butyl hydroperoxide, cumene hydroperoxide, disulfides, and combinations thereof.

8. A composition in accordance with any one of the preceding claims further comprising:

f) at least one filler.

10 9. A method for preparing a prepreg comprising

a) admixing a composition comprising

i) a polyphenyl ether having at least one vinyl end group;

ii) a styrene-butadiene copolymer; and

iii) an initiator; and

15 iv) a solvent

to form a varnish;

b) incorporating the varnish onto a substrate to form a coated
substrate;

20 c) drying the coated substrate at a drying temperature in the range of from 130°C to 160°C for an amount of time in the range of from 2 minutes to 6 minutes to form a prepreg.

10. A method in accordance with claim 9 wherein the composition of step a) further comprises v) a vinyl-benzyl ether of naphthol novolac.

11. A prepreg prepared by the method of claim 9.

25 12. A prepreg prepared by the method of claim 10.

13. An electrical laminate made from the prepreg of claim 11.

14. An electrical laminate made from the prepreg of claim 12.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2013/090010

A. CLASSIFICATION OF SUBJECT MATTER

C08F 299/00(2006.01)i; C08L 71/12(2006.01)i; C08L 25/10(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F; C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS,CNKI,WPI,EPODOC: DOWC,vinyl, +phenylene, ether, styrene, butadiene, crosslink+, cur+, glass transition temperature, Tg, dielectric constant, dissipation factor, vinyl-benzyl, naphthol novolac

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	CN 102807658 A (GUANGDONG SHENGYI SCI TECH CO) 05 December 2012 (2012-12-05) example 1	1-3,5-9,11,13
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X	US 2010080892 A1 (O'BRIEN MICHAEL JET AL.) 01 April 2010 (2010-04-01) claims 1-22	1-3,5-9,11,13
A	US 2006041086 A1 (BIRSAK JOOPET AL.) 23 February 2006 (2006-02-23) the whole document	1-14
A	WO 0140354 A1 (GEN ELECTRIC) 07 June 2001 (2001-06-07) the whole document	1-14
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

“A”	document defining the general state of the art which is not considered to be of particular relevance	“T”	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“E”	earlier application or patent but published on or after the international filing date	“X”	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“L”	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	“Y”	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“O”	document referring to an oral disclosure, use, exhibition or other means	“&”	document member of the same patent family
“P”	document published prior to the international filing date but later than the priority date claimed		

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International application No.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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