U.S. Patent Number 7,425,371 discloses a thermosetting resin system that appointed to be useful in the manufacture of high performance prepreg, laminate and composite materials as well as the prepregs, laminates and composites made from the thermosetting resin composition. The reference discloses modifications of CEs with SMA but this composition lacks the electrical performance for 4G and beyond applications, and no example is given to illustrate any benefit derived by modifying CE with SMA. The large part of electrical properties was achieved by blending fused silica with epoxy, ester, elastomers such as SMA, and a flame retardant. Furthermore, the compositions claimed a chemically blended product, not a reaction intermediate.

Accordingly, there remains a need in the art for ultra low loss dielectric thermosetting resin compositions for high performance laminates. Particularly needed in the art are ultra low loss dielectric thermosetting resin compositions for use in high performance and high layer count, multilayer printed circuit board (PCB), prepregs, resin coated copper (RCC), film adhesives, high frequency radomes, radio frequency (RF) laminates and various other composites made from resin compositions. Further needed in the art is a thermosetting resin composition that exhibits excellent dielectric properties suitable but not limited for 4G and 3rd Generation Partnership Project (3GPP).

SUMMARY ~~OF THE INVENTION~~

The present disclosure~~invention~~ provides ultra low loss dielectric thermosetting resin compositions for high performance laminates. Ultra low loss dielectric thermosetting resin

compositions are provided for use in high performance and high layer count, multilayer printed circuit board (PCB), prepregs, resin coated copper (RCC), film adhesives, high frequency radomes, radio frequency (RF) laminates and various other composites made from resin compositions. Further provided is a thermosetting resin composition that exhibits excellent dielectric properties suitable but not limited for 4G and 3rd Generation Partnership Project (3GPP).

More specifically, the ~~invention~~ disclosure provides a thermosetting resin having the form:

$$T_n\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}W]_{n-1}\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}(OCN)_f/(R)_{1-f}]_{n+2}$$

wherein "T" is a 1, 3, 5-substituted-triazine moiety (C_3N_3); "W" is a linking atom between triazine and either component A or component B; "Z" is component (A); "H" is component (B); "OCN" is cyanate ester end group; "R" is a reactive end group of component B; "n" is an integer greater than or equal to 1; and "f" is a weight or mole fraction of component A.

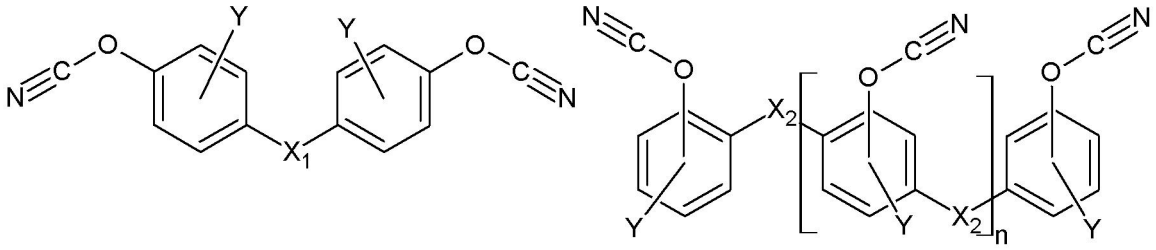
The ~~invention~~ disclosure provides a thermosetting resin composition via chemical attachment of:

a. at least one cyanate ester component (A);

b. at least one reactive intermediate component (B), said component B being capable of copolymerization with said component (A);

Component (A) is a member selected from the group consisting of 2, 2 –bis(4 – Cyanatophenyl) ispropylyidene, Bisphenol F Cyanate ester, Primaset PT resin, Primaset LECY and mixtures thereof. Preferably, component (A) is represented by the formula:

7a



wherein X_1 and X_2 individually represent R and R is a member selected from the group consisting of -$CH(CH_3)$-, -CH_2-, -$C(CH_3)_2$-, dicyclopentadiene (DCP), and functionalized DCP; n is an integer greater than 1; and Y represents at least one functional group.

Component B is a reactive modifier selected from the group consisting of thermoplastics, small organic molecules, rubbers, and inorganic/organometallic polymers.

In an aspect, there is provided a thermosetting resin composition represented by the formula:

$$T_n\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}W]_{n-1}\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}(OCN)_f/(R)_{1-f}]_{n+2}$$

wherein "T" is a 1, 3, 5-substituted-triazine moiety C_3N_3; "W" is an oxygen atom and is a linking atom between triazine and either component A or component B; "Z" is component A; "H" is component B; "OCN" is a cyanate ester end group of component A; "R" is a OH reactive end group of component B; "n" is an integer greater than or equal to 1; and "f" is a mole fraction of component A;

wherein said thermosetting resin composition is formed by chemical attachment of:

a. at least one cyanate ester component A;

b. at least one reactive intermediate component B, said component B being capable of copolymerization with said component A, said component B being a thermoplastic selected from the group consisting of (i) Hydrogenated hydroxylated polybutadiene (HHPBD), and (ii) polymethylphenylsiloxane containing between 3-9% OH functional groups.

In another aspect, there is provided a method of making a thermosetting resin composition, comprising the steps of:

a. selecting at least one cyanate ester component A

b. heating said component A to a given temperature for a time period;

c. selecting at least one reactive intermediate component B, said component B being capable of copolymerization with said component A, said component B a thermoplastic selected from the group consisting of (i) Hydrogenated hydroxylated polybutadiene (HHPBD) and (ii) polymethylphenylsiloxane containing between 3-9% OH functional groups;

d. heating component B;

e. adding component B to component A to form a reaction mixture;

f. heating said reaction mixture and stirring said reaction mixture to react components together to form a resin;

g. monitoring progress of said reaction by monitoring viscosity and refractive index of said resin at a reaction temperature, said reaction being complete when said viscosity of said resin at said reaction temperature is between 100 mPas and 200,000 mPas, wherein said resin is cooled to stop said reaction to yield a homogeneous resin of the formula:

$$T_n\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}W]_{n-1}\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}(OCN)_f/(R)_{1-f}]_{n+2}$$

wherein T is a 1, 3, 5-substituted-triazine moiety C_3N_3; W is an oxygen atom and is a linking atom between triazine and either component A or component B; Z is component A; H is component B; OCN is a cyanate ester end group of component A; R is a OH reactive end group of component B; n is an integer greater than or equal to 1; and f is a mole fraction of component A.

DETAILED DESCRIPTION OF THE INVENTION

The subject invention provides a thermosetting resin composition that exhibits excellent dielectric properties suitable but not limited for 4G and 3rd Generation Partnership Project (3GPP), which is a major enhancement of the Long Term Evolution (LTE) standard. 4G-LTE-Advanced offers a new wave of mobile functionality that will propel mobile speed and quality well into the future. 4G-LTE-Advanced offers peak data rates of 1 Gbps compared to 300 Mbps on 4G-LTE and 10X-30X faster download speeds than its predecessor. This speed can only be possible through the combination of new software and hardware and new ultra – low DK/Df materials, which play a significant role in maintaining signal integrity. The power amplifer boards for 4G LET base station and back-panel in server, network gear, and Wi-Fi, require substrates with low Dk/Df for new communication technologies. Besides electrical properties, compositions providing excellent thermal, mechanical and other physical properties

CLAIMS

What is claimed is:

1. A thermosetting resin composition ~~having~~ represented by the formula:

$$T_n\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}W]_{n-1}\text{-}[W\text{-}(Z)_f/(H)_{1-f}\text{-}(OCN)_f/(R)_{1-f}]_{n+2}$$

wherein "T" is a 1, 3, 5-substituted-triazine moiety ~~(~~C_3N_3~~)~~; "W" is an oxygen atom and is a linking atom between triazine and either component A or component B; "Z" is component ~~(~~A~~)~~; "H" is component ~~(~~B~~)~~; "OCN" is a cyanate ester end group of component A; "R" is a OH reactive end group of component B; "n" is an integer greater than or equal to 1; and "f" is a ~~weight or~~ mole fraction of component A;

wherein said thermosetting resin composition is formed by chemical attachment of:

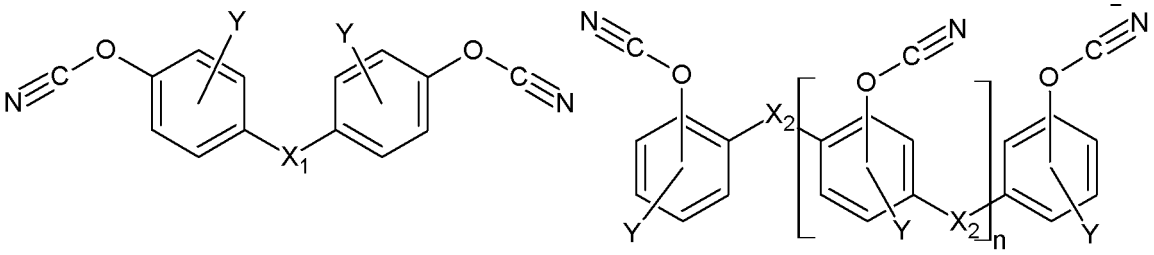
a. at least one cyanate ester component ~~(~~A~~)~~;

b. at least one reactive intermediate component ~~(~~B~~)~~, said component B being capable of copolymerization with said component ~~(~~A~~)~~, said component B being a thermoplastic selected from the group consisting of (i) Hydrogenated hydroxylated polybutadiene (HHPBD), and (ii) polymethylphenylsiloxane containing between 3-9% OH functional groups.

2. ~~A~~The thermosetting resin composition ~~as recited by~~of claim 1, wherein said component ~~(~~A~~)~~ is ~~a member~~ selected from the group consisting of 2,~~–~~2~~–~~bis(4~~–~~c~~C~~yanatophenyl) ispropylyidene, Bisphenol F c~~C~~yanate ester, Bisphenol E c~~C~~yanate ester , Bisphenol M c~~C~~yanate ester~~–~~, dicyanate of Oxydiphenol~~–~~,~~,~~ resorcinol c~~C~~yanate ester~~–~~, ~~C~~cyanated novolac~~–~~,

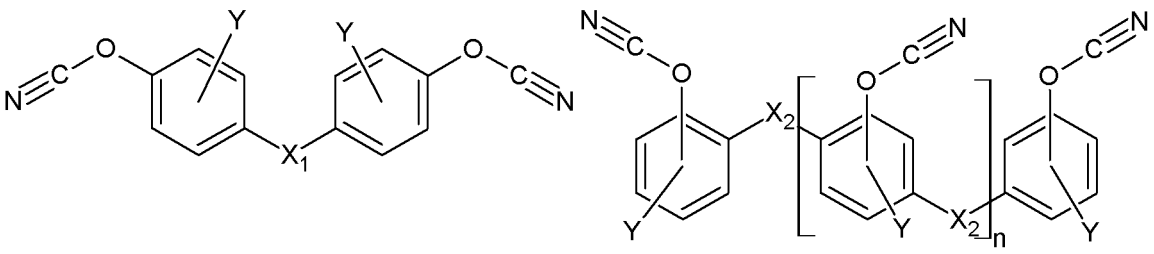
cCyanated phenol—diclopentadine–, diphenyl cyanate ester–, naphthol aralkyl Ccyanate ester, and mixtures thereof.

3. AThe thermosetting resin composition as recited byof claim 1, wherein said component (A) is defined by the formula



wherein X_1 and X_2 individually represent R, and R is a member selected from the group consisting of -$CH(CH_3)$-, -CH_2-, -$C(CH_3)_2$-, dicyclopentadiene (DCP), and functionalized DCP; n is an integer greater than 1; and Y represents at least one functional group Ar, SO_2, O, or S; n is an integer greater than 1; and Y represents at least one functional group; and wherein Ar is selected from the group consisting of a functionalized or non-functionalized benzene, biphenyl, naphthalene, phenol novolac, bisphenol A, bisphenol A novolac, bisphenol F, and bisphenol F novolac.

4. A thermosetting resin composition as recited by claim 1, wherein said component (A) is defined by the formula



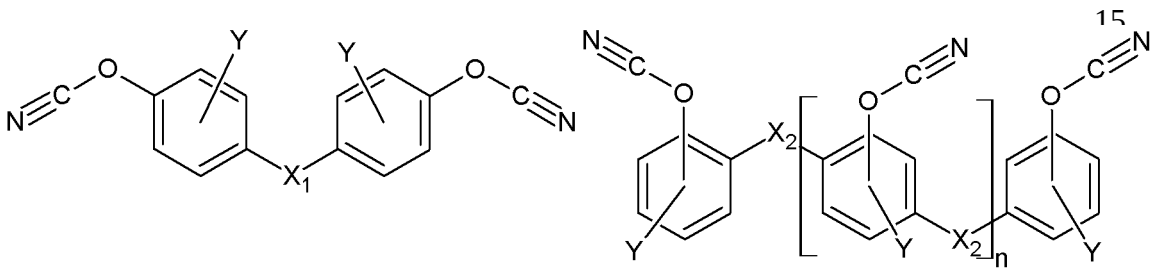
~~wherein X_1 and X_2 individually represent at least R, Ar, SO_2, O, or S; n is an integer greater than 1; and Y represents at least one functional group.~~

~~5. A thermosetting resin composition as recited by claim 4, wherein R is a member selected from the group consisting of $-CH(CH_3)-$, $-CH_2-$, $-C(CH_3)_2-$, dicyclopentadiene (DCP), and functionalized DCP.~~

~~6. A thermosetting resin composition as recited by claim 4, wherein Ar is a member selected from the group consisting of a functionalized or non-functionalized benzene, biphenyl, naphthalene, phenol novolac, bisphenol A, bisphenol A novolac, bisphenol F, and bisphenol F novolac.~~

~~7.~~4. ~~A~~The thermosetting resin composition ~~as recited by~~of claim ~~4~~3, wherein Y is ~~a member~~ selected from the group consisting of hydrogen, aliphatic groups, aromatic groups, and halogens.

~~8. A thermosetting resin composition as recited by claim 1, wherein said component (A) is defined by the formula~~



~~wherein X_1 is R, Ar, SO_2, O, or S; n is an integer greater than 1; and Y represents at least one functional group.~~

~~9. A thermosetting resin composition as recited by claim 8, wherein R is a member selected from the group consisting of -CH(CH$_3$)-, -CH$_2$-, -C(CH$_3$)$_2$-, dicyclopentadiene (DCP), and functionalized DCP.~~

~~10. A thermosetting resin composition as recited by claim 8, wherein Ar is a member selected from the group consisting of a functionalized or non-functionalized benzene, biphenyl, naphthalene, phenol novolac, bisphenol A, bisphenol A novolac, bisphenol F, and bisphenol F novolac.~~

~~11. A thermosetting resin composition as recited by claim 8, wherein Y is a member selected from the group consisting of hydrogen, aliphatic groups, aromatic groups, and halogens.~~

~~12. A thermosetting resin composition as recited by claim 8, wherein said wherein X$_2$ is R, Ar, SO$_2$, O, or S.~~

~~13.~~5. ~~A~~ The thermosetting resin composition ~~as recited by~~of claim 1, wherein Z has a wt% of at least 50% in reaction with component B.

~~14. A thermosetting resin composition as recited by claim 1, wherein component B is a reactive modifier selected from the group consisting of thermoplastics, small organic molecules, rubbers, and inorganic/organometallic polymers.~~

~~15.~~6. ~~A~~The thermosetting resin composition ~~as recited by~~of claim 1~~4~~ comprising secondary reactive groups selected from the group consisting of allyls, vinyls, acrylates, halogens, ethyoxys, and methoxys.

~~16. A thermosetting resin composition as recited by claim 14, wherein said thermoplastic additives are selected from the group consisting of (i) hydroxylated polybutadiene (HPBD) with molecular weights between 100 and 10 000 g/mol, (ii) Hydrogenated hydroxylated polybutadiene (HHPBD), (iii) reactive polydimethylsiloxane (PDMS) with molecular weights between and including 100 – 20 000 g/mol and at least 2 functional groups per molecule of either hydroxyl or epoxy groups, or (iv) polymethylphenylsiloxane containing between 3-9% OH functional groups.~~

~~17.~~7. ~~A~~The thermosetting resin composition ~~as recited by~~of claim 1, wherein the reactive end group R of component B is ~~a member~~ selected from the group consisting of OH, SH, NH_2, Allyl, Vinyl, Phenol, Anhydrides, Carboxylic acids and Acetylenes.

~~18.~~8. ~~A~~ The thermosetting resin composition ~~as recited by~~of claim 1, wherein component B ranges from about 5%-50% by wt, preferably wherein component B ranges from about 20%-35% by wt.

~~19. A thermosetting resin composition as recited by claim 1, wherein component B ranges from about 20%-35% by wt.~~

~~20.~~9. The~~A~~ thermosetting resin composition ~~as recited by~~of claim 1, wherein content of each component in said resin comprises 50 – 95 wt% component A, 5 – 50 wt % component B, and up to 30 wt % flame-retardant.

~~21.~~10. ~~A~~The ~~–~~ thermosetting resin composition as defined in claim 1, having a dielectric constant and low dielectric loss for use in multilayer printed circuit boards for high-speed analog and digital circuitry applications, wherein said dielectric constant and dielectric loss

[DK/Df] from subsection c is dependent on the ratio of weight percent of component A and component Bcomprising: .

T_n [W (Z)$_f$/(H)$_{1-f}$ W]$_{n-1}$ [W (Z)$_f$/(H)$_{1-f}$ (OCN)$_f$/(R)$_{1-f}$]$_{n+2}$

wherein "T" is a 1, 3, 5-substituted-triazine moiety (C_3N_3); "W" is a linking atom between triazine and either component A or component B; "Z" is component (A); "H" is component (B); "OCN" is cyanate ester end group; "R" is a reactive end group of component B; "n" is an integer greater than or equal to 1; and "f" is a weight or mole fraction of component A;

wherein said thermosetting resin composition is formed by chemical attachment of:

y. at least one cyanate ester component (A);

z. at least one reactive intermediate component (B), said component B being capable of copolymerization with said component (A).

wherein said dielectric constant and dielectric loss [DK/Df] from subsection c is dependent on the ratio of weight percent of component (A) and component (B).

28.11. AThe thermosetting resin composition as recited byof claim 1021, wherein said thermosetting resin composition is used for prepregs / pre-impregnated composite fibers and adhesives.

29.12. AThe thermosetting resin composition as recited byof claim 2211, wherein said prepreg / pre-impregnated composite fibres are converted to laminates, wherein one or more prepreg layers are stacked-up between one or more sheets of conductive foil.

~~30.~~13. ~~A~~ The thermosetting resin composition ~~as recited by~~of claim ~~21~~10, wherein said dielectric constant and dielectric loss [DK/DF] is < 2.2 / 0.0008 at 3 - 10 GHZ range and said component (B) has a weight percent of greater than 35%.

~~31.~~14. A method of making a thermosetting resin composition, comprising the steps of:

a. selecting at least one cyanate ester component ~~(~~A~~)~~

b. heating said component ~~(~~A~~)~~ to a given temperature for a time period;

c. selecting at least one reactive intermediate component ~~(~~B~~)~~, said component B being capable of copolymerization with said component ~~(~~A~~)~~, said component B a thermoplastic selected from the group consisting of (i) Hydrogenated hydroxylated polybutadiene (HHPBD) and (ii) polymethylphenylsiloxane containing between 3-9% OH functional groups;

d. heating component ~~(~~B~~)~~;

e. adding component ~~(~~B~~)~~ to component ~~(~~A~~)~~ to form a reaction mixture;

f. heating said reaction mixture and stirring said reaction mixture to react components together to form a resin;

g. monitoring progress of said reaction by monitoring viscosity and refractive index of said resin at a reaction temperature, said reaction being complete when said viscosity of said resin at said reaction temperature is between 100 ~~cP~~mPas and 200,000 ~~cP~~mPas, wherein said resin is cooled to stop said reaction to yield a homogeneous resin of the formula:

T_n-[W-$(Z)_f$/$(H)_{1-f}$-W]$_{n-1}$-[W-$(Z)_f$/$(H)_{1-f}$-$(OCN)_f$/$(R)_{1-f}$]$_{n+2}$

wherein T is a 1, 3, 5-substituted-triazine moiety ~~(~~C_3N_3~~)~~; W is an oxygen atom and is a linking atom between triazine and either component A or component B; Z is component ~~(~~A~~)~~; H is component ~~(~~B~~)~~; OCN is a cyanate ester end group of component A; R is a OH reactive end group of component B; n is an integer greater than or equal to 1; and f is a ~~weight or~~ mole fraction of component A.

~~32.~~15. ~~A~~The method of ~~making a thermosetting resin composition as recited by~~ claim ~~25~~14, wherein said component ~~(~~A~~)~~ is heated to temperatures between 135 °C and 200 °C for between 1 and 5 hours.

~~33.~~16. ~~A~~The method of ~~making a thermosetting resin composition as recited by~~ claim ~~25~~14, wherein said component ~~(~~B~~)~~ is heated to about 130 °C and added into component ~~(~~A~~)~~.

~~34.~~17. ~~A~~The method of ~~making a thermosetting resin composition as recited by~~ claim ~~25~~14, wherein said reaction mixture is heated to between 100 °C and 195 °C.

~~35.~~18. ~~A~~The method of ~~making a thermosetting resin composition as recited by~~ claim ~~25~~14, wherein said resin is completed when said viscosity of the resin at 95 °C is between 100 ~~cP~~mPas and 200,000 ~~cP~~mPas.

~~36.~~19. ~~A~~The method of ~~making a thermosetting resin composition as recited by~~ claim ~~25~~14, wherein at room temperature said viscosity of said resin ranges between 50 - 1000 ~~cP~~mPas.

~~37. A method of making a thermosetting resin composition as recited by claim 25, wherein component B is a reactive modifier selected from the group consisting of thermoplastics, small organic molecules, rubbers, and inorganic/organometallic polymers.~~