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(54) **ASSEMBLIES USEFUL FOR THE  
PREPARATION OF ELECTRONIC  
COMPONENTS AND METHODS FOR  
MAKING SAME**

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(57) **ABSTRACT**

In accordance with the present invention, assemblies have been developed which are useful for a variety of applications, e.g., in RF applications where low electrical loss products are desirable, e.g., in cellular communications, RF antennas, satellite communications, radar, power amplifiers, high speed digital applications, laminate-based chip carriers, and the like. Invention assemblies comprise a combination of a first reinforced thermoplastic-containing layer and a first non-reinforced thermoplastic-containing layer, wherein the reinforced and non-reinforced thermoplastic-containing layers are capable of forming a bond (e.g., a cohesive or adhesive bond) therebetween, thereby providing performance properties (e.g., electrical performance and cladding bond strength) that are superior to the performance properties of either material alone. The reinforced thermoplastic-containing layer can include a porous substrate impregnated with a composition comprising: a first component (i.e., a low loss, low dielectric constant, hydrocarbyl thermoplastic), a second component (i.e., a component able to crosslink and produce a thermoset in the presence of the first component), and a free radical source. Also provided in accordance with the present invention are methods for preparing the above-described assemblies.

**ASSEMBLIES USEFUL FOR THE PREPARATION OF ELECTRONIC COMPONENTS AND METHODS FOR MAKING SAME**

**FIELD OF THE INVENTION**

[0001] The present invention relates to assemblies and laminate structures, methods for making same, and uses thereof. Invention assemblies and laminate structures are useful, for example, in the preparation of components used in RF applications, applications where low electrical loss products are required, e.g., in cellular telecommunications, RF antennas, satellite communications, radar, power amplifiers, high speed digital applications, laminate-based chip carriers, and the like.

**BACKGROUND OF THE INVENTION**

[0002] Laminate structures employed in cellular telecommunications, laminate-based chip carriers, and the like, must meet a number of physical and electrical performance criteria, e.g., low loss, low dielectric constant, good heat resistance, good dimensional stability, low density, and the like.

[0003] Historically, in the production of printed circuit boards used as antennas and other elements of cellular and wireless infrastructure, conventional woven glass laminates based on PTFE (polytetrafluoroethylene) have been utilized. While these are readily and conveniently manufactured using technology well known to those of skill in the art, they tend to be expensive and heavy (having a density of about 2.5).

[0004] Thermoplastic resins are commonly used for the preparation of substrates for laminate and prepreg systems. However, thermoplastics frequently have limitations which may preclude their use as a substrate material in foil-clad laminate structures. These limitations may include insufficient thermo-mechanical stability and an inability to form a sufficient bond with the foil cladding.

[0005] Thermoplastic materials used in the preparation of laminate and prepreg systems preferably have glass and melt transition temperatures which are higher than the maximum temperatures achieved during processing of the substrate (e.g., the temperature achieved for processing of a printed circuit board). However, such thermoplastic materials are frequently expensive.

[0006] Preparation of foil-clad laminate thermoplastic structures is often difficult as it is generally difficult to form a bond between a metal foil and the surface of the substrate. A variety of factors, including molecular composition and structure, may influence the ability to form a foil layer on a thermoplastic substrate surface.

[0007] Reinforcement of substrate layer is desirable and known in the art. Preferably, a thermally-resistant reinforcement is added to a thermoplastic polymer to form a composite substrate. One method for adding reinforcement to the substrate includes uniformly blending microfibers into the polymer for the preparation of the substrate. However, the amount of microfiber that may be incorporated into a substrate by this method is limited.

[0008] An alternate method for preparing a reinforced substrate is to coat a fabric-like reinforcement with a thermoplastic polymer. However, this method has limitations as this route of preparation may be limited to co-extrusion,

which can be difficult to perform with light-weight reinforcements, as are typically required for use with PCB substrates.

[0009] In view of the high demand and widespread use of such laminate structures, in addition to meeting the above-described performance properties (i.e., a low dielectric constant, low weight and low loss), it is further desirable that such materials can be prepared from relatively inexpensive starting materials employing readily scalable, low cost processes. The present invention addresses these and other needs as described in greater detail herein.

**SUMMARY OF THE INVENTION**

[0010] In accordance with the present invention, there are provided novel assemblies and laminate structures, methods for the preparation thereof, and various uses therefor. Invention materials are useful, for example, in the preparation of components used in RF applications, applications where low electrical loss products are required, e.g., in cellular telecommunications, RF antennas, satellite communications, radar, power amplifiers, high speed digital applications, laminate-based chip carriers, and the like.

**DETAILED DESCRIPTION OF THE INVENTION**

[0011] In accordance with one aspect of the present invention, there are provided assemblies comprising: (a) a first reinforced thermoplastic-containing layer and (b) a first non-reinforced thermoplastic layer, wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of interacting sufficiently so as to form a bond therebetween, wherein said first reinforced thermoplastic-containing layer comprises a porous substrate impregnated with a composition comprising:

- [0012] (a) a first component comprising a low loss, low dielectric constant, hydrocarbyl thermoplastic resin,
- [0013] (b) a second component which is capable of crosslinking to produce a thermoset in the presence of the first component,
- [0014] (c) a free radical source,
- [0015] (d) optionally, one or more additives, and
- [0016] (e) an optional diluent therefore,

wherein the resulting impregnated substrate has been subjected, if necessary, to conditions suitable to remove substantially all of the optionally present diluent therefrom.

[0017] As employed herein, the term "assembly" refers to a structure comprising at least one reinforced thermoplastic layer and at least one non-reinforced thermoplastic layer for use in the preparation of a multilayer structure.

[0018] As employed herein, the term "reinforced thermoplastic-containing layer" (or "prepreg") refers to a porous substrate which is impregnated with a composition which includes a thermoplastic and thermoset resin. Optionally, the thermoset resin is partially cured, and may also include fillers and/or additives. Exemplary reinforced thermoplastic containing layers are described, for example, in U.S. Ser. No. 11/006,211, filed Dec. 6, 2004, which is incorporated by reference herein in its entirety.

[0019] As employed herein, the term "porous substrate" refers to a woven or non-woven substrate which can include, but is not limited to, woven glass, non-woven glass, woven aramid fibers, non-woven aramid fibers, woven liquid crystal polymer fibers, non-woven liquid crystal polymer fibers,

woven synthetic polymer fibers, non-woven synthetic polymer fibers, randomly dispersed fiber reinforcements, expanded polytetrafluoroethylene (PTFE) structures and combinations of any two or more thereof. Specifically, materials contemplated for use as the "porous substrate" can include, but are not limited to, fiberglass, quartz, polyester fiber, polyamide fiber, polyphenylene sulfide fiber, polyetherimide fiber, cyclic olefin copolymer fiber, polyalkylene fiber, liquid crystalline polymer, poly(p-phenylene-2,6-benzobisoxazole), copolymers of polytetrafluoroethylene and perfluoromethylvinyl ether (MFA) and combinations of any two or more thereof.

**[0020]** As employed herein, "combination," when used to refer to polymers, embraces blends, copolymers, coplanar layers, and the like, of any two or more of the polymer or resin materials.

**[0021]** As employed herein, the term "non-reinforced thermoplastic-containing layer" refers to a substrate which includes a thermoplastic resin and does not include a porous substrate.

**[0022]** As employed herein, the term "thermoplastic polymers" refers to polymers which will repeatedly soften when heated and harden when cooled. In addition, thermoplastic polymers may melt and possibly flow at elevated temperatures. Exemplary thermoplastic polymers suitable for use in the present invention can include, but are not limited to, cyclic olefin copolymers, terpolymers, block copolymers, or combinations of any two or more thereof.

**[0023]** The thermoplastic polymer or resin employed for the reinforced and non-reinforced layers may be the same or may be different. Preferably, the thermoplastic polymers for the reinforced and non-reinforced layers have similar glass transition temperatures and coefficients of thermal expansion. In preferred embodiments, the thermoplastic resin is selected from cyclic olefin copolymers, polyetherimides, polyether ether ketones (PEEKs), liquid crystal polymers (LCPs), polytetrafluoroethylene, polyphenylenesulfide, polyphenyleneoxide, polyphenylene ether, polymethylpentene (TPX), polypropylene, and polyethylene.

**[0024]** The thickness of the non-reinforced thermoplastic layer can vary widely, typically falling in the range of about 10 up to about 3000 microns or higher. In preferred embodiments, the non-reinforced thermoplastic layer has a thickness of at least 25 microns, up to about 1300 microns. In especially preferred embodiments, the reinforced thermoplastic layer has a thickness of at least 25 microns up to about 400 microns.

**[0025]** As readily recognized by those of skill in the art, the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer can interact to form a bond therebetween in a variety of ways. For example, the layers may interact as a result of having compatible melt solubility properties. Alternatively, the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of interacting to form an adhesive bond therebetween. As yet another alternative, the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of interacting to form a mechanical bond therebetween. As still another alternative, the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer interact sufficiently, regardless of the mechanism of interaction, to produce an interlayer peel strength of at least about four pounds per linear inch.

**[0026]** As employed herein, the term "cohesive bond" refers to the intramolecular attractive forces which hold two or more bodies of like composition together.

**[0027]** As employed herein, the term "adhesive bond" refers to the forces, such as dipole bonds, which attract adhesives and base materials to each other.

**[0028]** As employed herein, the term "low loss" refers to materials which cause minimal energy dissipation when associated with electromagnetic signal transmission.

**[0029]** As employed herein, the term "dielectric constant" refers to the permittivity of a volume of material relative to that same volume of free space. Preferably, inventive materials have a dielectric constant of less than about 4.5, more preferably less than 3.0, and even more preferably close to about 2.5.

**[0030]** As employed herein, "about" means in quantitative terms plus or minus 10%.

**[0031]** As employed herein, "thermoset" refers to a polymer or resin material which cures (sets) by a chemical reaction. Optionally, the thermoset may also require heat and/or pressure.

**[0032]** As employed herein, the term "hydrocarbyl thermoplastic resins" refers to polymeric materials which are prepared from non-heteroatom containing, unsaturated hydrocarbons, e.g., polyolefins, co-polymers including olefin monomers, cyclic olefin monomers, and the like, terpolymers, block copolymers, and the like.

**[0033]** Low loss, low dielectric constant, hydrocarbyl thermoplastic resins contemplated for use in the practice of the present invention can be characterized, for example, as materials which, when laminated, have a dielectric constant  $\leq 4.5$  nominal, and an electrical loss tangent  $\leq 0.02$ . Preferably, the dielectric constant of the assembly is between 2.0 and 4.5. Additionally, such materials contemplated for use in the practice of the present invention may further be characterized as having a glass transition temperature  $\geq 80^\circ$  C. Optionally, low loss, low dielectric constant, hydrocarbyl thermoplastic materials contemplated for use in the practice of the present invention may be further characterized as being capable of undergoing further crosslinking. For example, such materials can be rendered capable of undergoing further crosslinking by the presence of residual unsaturation thereon. Alternatively, the low loss, low dielectric constant, hydrocarbyl thermoplastic resin can be rendered crosslinkable by the presence of one or more crosslinkable substituents thereon.

**[0034]** Exemplary low loss, low dielectric constant, hydrocarbyl thermoplastic resins contemplated for use in the practice of the present invention include cyclic olefin-containing copolymers, terpolymers, block copolymers, or combinations of any two or more thereof. Examples of cyclic olefin-containing copolymers include copolymers of an aliphatic olefin and a cyclic olefin, copolymers of an olefin and norbornene, and the like.

**[0035]** As readily recognized by those of skill in the art, the above-described copolymers can be synthesized in a variety of ways, e.g., by addition polymerization, by ring opening polymerization of norbornene with an olefin, and the like.

**[0036]** The molar ratio of olefin to norbornene can vary widely, typically falling in the range of about 1:6 up to about 1:1.5.

**[0037]** The molecular weight of cyclic olefin-containing copolymers contemplated for use in the practice of the



to cycloalkenylene groups further bearing one or more substituents as set forth above.

**[0057]** As employed herein, “oxyalkylene” refers to the divalent moiety —O-alkylene-, wherein alkylene is as defined above, and “substituted oxyalkylene” refers to oxyalkylene groups further bearing one or more substituents as set forth above.

**[0058]** As employed herein, “oxyalkenylene” refers to the divalent, ene-functionalized moiety —O-alkenylene-, wherein alkenylene is as defined herein, and “substituted oxyalkenylene” refers to oxyalkenylene groups further bearing one or more substituents as set forth above.

**[0059]** As employed herein, “alkenylene” refers to divalent, straight or branched chain hydrocarbyl groups having at least one carbon-carbon double bond, and having in the range of about 2 up to 12 carbon atoms, and “substituted alkenylene” refers to alkenylene groups further bearing one or more substituents as set forth above.

**[0060]** As employed herein, “alkynylene” refers to divalent linear or branched chain hydrocarbyl groups having at least one carbon-carbon triple bond, and having in the range of about 2 up to 12 carbon atoms, and “substituted alkynylene” refers to alkynylene groups further bearing one or more substituents as set forth above.

**[0061]** As employed herein, “arylene” refers to divalent aromatic groups having in the range of 6 up to 14 carbon atoms and “substituted arylene” refers to arylene groups further bearing one or more substituents as set forth above.

**[0062]** As employed herein, “alkylarylene” refers to alkyl-substituted arylene groups and “substituted alkylarylene” refers to alkylarylene groups further bearing one or more substituents as set forth above.

**[0063]** As employed herein, “arylalkylene” refers to aryl-substituted alkylene groups and “substituted arylalkylene” refers to arylalkylene groups further bearing one or more substituents as set forth above.

**[0064]** As employed herein, “arylalkenylene” refers to aryl-substituted alkenylene groups and “substituted arylalkenylene” refers to arylalkenylene groups further bearing one or more substituents as set forth above.

**[0065]** As employed herein, “arylalkynylene” refers to aryl-substituted alkynylene groups and “substituted arylalkynylene” refers to arylalkynylene groups further bearing one or more substituents as set forth above.

**[0066]** Presently preferred components contemplated for use in the practice of the present invention which are capable of crosslinking to produce a thermoset include thermally stable dielectric materials such as di-allylic compound(s), tri-allylic compound(s), di-vinyl compound(s), tri-vinyl compound(s), conjugated diene(s), non-conjugated diene(s), di(meth)acrylate compound(s), tri(meth)acrylate compound(s), and the like, as well as mixtures of any two or more thereof.

**[0067]** Especially preferred components capable of crosslinking to produce a thermoset contemplated for use in the practice of the present invention include triallyl isocyanurate, triallyl cyanurate, 1,2,4-trivinylcyclohexane, 1,9-decadiene, 1,7-octadiene, and the like, as well as mixtures of any two or more thereof.

**[0068]** As readily recognized by those of skill in the art, the weight ratio between component (a) and component (b) of invention compositions can vary widely. Typically, such ratio falls in the range of about 1:1 up to about 100:1. In preferred embodiments, the weight ratio between compo-

nent (a) and component (b) of invention compositions falls in the range of about 1.5:1 up to about 99:1.

**[0069]** Free radical sources contemplated for use in the practice of the present invention (i.e., component (c)) can be either thermally or photochemically activated. Free radical sources that are capable of being activated thermally include peroxides, azo compounds, redox initiators, azides, and the like, as well as mixtures of any two or more thereof.

**[0070]** Presently preferred peroxides are those having a decomposition temperature of at least about 50° C. Exemplary peroxides contemplated for use in the practice of the present invention include ketone peroxides (e.g., methyl ethyl ketone peroxide, cyclohexanone peroxide, and the like), peroxyketals (e.g., 1,1-bis(t-butyl peroxy)-3,3,5-trimethylcyclohexane, 2,2-bis(t-butyl peroxy)butane, and the like), hydroperoxides (e.g., t-butyl hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, and the like), dialkyl peroxides (e.g., dicumyl peroxide, 2,5-dimethyl-2,5-di(t-butyl peroxy)hexyne-3,  $\alpha,\alpha'$ -bis(t-butyl peroxy-m-isopropyl)benzene, and the like), diacyl peroxides (e.g., octanoyl peroxide, isobutyryl peroxide, and the like), peroxyesters (e.g., peroxydicarbonate), and the like.

**[0071]** An exemplary azo compound contemplated for use in the practice of the present invention is  $\alpha,\alpha'$ -azobis(isobutyronitrile).

**[0072]** Exemplary redox initiators contemplated for use in the practice of the present invention include combinations of peroxides (e.g.,  $H_2O_2$ ) and a ferrous salt, and the like.

**[0073]** An exemplary azide contemplated for use in the practice of the present invention is acetyl azide.

**[0074]** Exemplary compounds contemplated for use in this aspect of the present invention include benzophenone, 9-phenyl acridine, ethyl Michler's ketone (EMK), zinc acetylacetonate, triphenyl phosphine oxide, and the like, as well as mixtures of any two or more thereof.

**[0075]** As readily recognized by those of skill in the art, the amount of free radical source incorporated into invention compositions can vary widely. Typically, the amount of component (c) employed in invention compositions will fall in the range of about 0.01-10 weight percent, based on the total weight of the composition.

**[0076]** Optional additives contemplated for use in the practice of the present invention include fire retardants, fillers, fluorescent dyes, pigments, flow modifiers, plasticizers, cure retardants, cure accelerators, strength enhancers, UV protectors (especially UV blocking dyes appropriate to enable Automatic-Optical Inspection (AOI) of Circuitry), and the like, as well as mixtures of any two or more thereof.

**[0077]** Fire retardants contemplated for use in the practice of the present invention include substantially halogen-free fire retardants, halogenated fire retardants, phosphorus-containing fire retardants, additive and/or reactive flame retardants which may serve as intumescent or char formers, silanes, siloxanes, low melting glasses, zinc-, boron-, aluminum-, or magnesium-based fire retardants, and the like.

**[0078]** Specific compounds contemplated for use as fire retardants include phosphites, phosphates (e.g., butylated triphenyl phosphate, ammonium polyphosphate (APP), and the like), phosphonates, nitrogenes (e.g., melamine derivatives), bromine-containing fire retardants (e.g., brominated styrenes), zinc- and/or boron-based fire retardants (e.g., zinc borate, zinc stannate, borax, and the like), aluminum-based fire retardants (e.g., aluminum trihydrate (ATH)), magne-

sium-based fire retardants (e.g., magnesium hydroxide), and the like, as well as combinations of any two or more thereof.

**[0079]** Fillers contemplated for use in the practice of the present invention can be either organic or inorganic. Exemplary fillers include ceramic fillers (which provide dimensional stability), fused silica, glass bubbles, glass spheres, chopped glass, polymeric spheres, polymeric bubbles, and the like, as well as combinations of any two or more thereof.

**[0080]** Fillers contemplated for optional use in the practice of the present invention may optionally be conductive (electrically and/or thermally). Electrically conductive fillers contemplated for use in the practice of the present invention include, for example, silver, nickel, gold, cobalt, copper, aluminum, graphite, silver-coated graphite, nickel-coated graphite, alloys of such metals, and the like, as well as mixtures thereof. Both powder and flake forms of filler may be used in the compositions of the present invention. Preferably, the flake has a thickness of less than about 2 microns, with planar dimensions of about 20 to about 25 microns. Flake employed herein preferably has a surface area of about 0.15 to 5.0 m<sup>2</sup>/g and a tap density of about 0.4 up to about 5.5 g/cc. It is presently preferred that powder employed in the practice of the invention has a diameter of about 0.5 to 15 microns. If present, the filler typically comprises in the range of about 30% up to about 70% by weight of the adhesive formulation.

**[0081]** Thermally conductive fillers contemplated for optional use in the practice of the present invention include, for example, aluminum nitride, boron nitride, silicon carbide, diamond, graphite, beryllium oxide, magnesia, silica, alumina, and the like. Preferably, the particle size of these fillers will be about 20 microns. If aluminum nitride is used as a filler, it is preferred that it be passivated via an adherent, conformal coating (e.g., silica, or the like).

**[0082]** Fillers that are not electrical conductors may be used in the practice of the present invention. Such fillers may be desirable to impart some other property to the composition according to the invention, such as, for example, reduced thermal expansion of the cured material, increased or reduced dielectric constant, improved toughness, increased hydrophobicity, and the like. Examples of such fillers include perfluorinated hydrocarbon polymers (i.e., TEFLON<sup>TM</sup>), thermoplastic polymers, thermoplastic elastomers, mica, fused silica, glass powder, titanium dioxide, strontium oxide, and the like.

**[0083]** Dyes contemplated for use in certain embodiments of the present invention include nigrosine, Orasol blue GN, phthalocyanines, Fluoral green gold dye, and the like. When used, organic dyes in relatively low amounts (i.e., amounts less than about 0.2% by weight) provide contrast.

**[0084]** Pigments contemplated for use in certain embodiments of the present invention include any particulate material added solely for the purpose of imparting color to the formulation, e.g., carbon black, metal oxides (e.g., Fe<sub>2</sub>O<sub>3</sub>, titanium oxide), and the like. When present, pigments are typically present in the range of about 0.5 wt. % up to about 5 wt. %, relative to the base formulation.

**[0085]** Flow modifiers may optionally be employed in the practice of the present invention to alter the resin flow in order to facilitate achieving desired fill and/or lamination properties. Use of such optional additives may thereby (1) enhance intra-laminar adhesion and/or (2) produce a multi-layered board by bonding resinous prepregs to layers comprising etched circuitry. When employed in accordance with

the present invention, such additives are likely to be used at minimum loading levels (e.g., in the range of about 1 up to about 10 weight percent, based on the total weight of the formulation) to gain the benefit such additives can impart (e.g., enhanced heat and pressure induced flow) without compromising other physical and electrical properties.

**[0086]** Flow modifiers contemplated for use herein may be non-reactive or reactive (i.e., capable of participating in oxidative cross-linking). Such materials will desirably exhibit electrical and physical properties which are compatible with all of the components of the above-described compositions.

**[0087]** Exemplary flow modifiers contemplated for use in the practice of the present invention include monomeric, oligomeric, or polymeric (i.e., thermoplastic) saturated (aliphatic) hydrocarbons, unsaturated hydrocarbons, and the like.

**[0088]** Plasticizers (also called flexibilizers) contemplated for use in certain embodiments of the present invention include compounds that reduce the brittleness of the formulation, such as, for example, branched polyalkanes or polysiloxanes that lower the glass transition temperature (T<sub>g</sub>) of the formulation. Such plasticizers include, for example, polyethers, polyesters, polythiols, polysulfides, and the like. Plasticizers, when employed, are typically present in the range of about 0.5 wt. % up to about 30 wt. % of the formulation.

**[0089]** Cure retardants (also known as cell size regulators or quenching agents) contemplated for use in certain embodiments of the present invention include compounds which form radicals of low reactivity, such as, for example, silicone surfactants (generally), and the like.

**[0090]** Cure accelerators contemplated for use in certain embodiments of the present invention include compounds which enhance the rate of cure of the base polymer system, such as, for example, catalytically active materials, water, and the like.

**[0091]** Strength enhancers contemplated for use in certain embodiments of the present invention include compounds which increase the performance properties of the polymeric material to which they are added, such as, for example, crosslinking agents, and the like.

**[0092]** UV protectors contemplated for use in certain embodiments of the present invention include compounds which absorb incident ultraviolet (UV) radiation, thereby reducing the negative effects of such exposure on the resin or polymer system to which the protector has been added. Exemplary UV protectors include bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate, silicon, powdered metallic compounds, hindered amines (known in the art as "HALS"), and the like.

**[0093]** Optional diluents contemplated for use in the practice of the present invention include aromatic, aliphatic, cycloaliphatic, and the like, as well as combinations of any two or more thereof. Presently preferred diluents contemplated for optional use in the practice of the present invention are relatively non-polar. Exemplary diluents contemplated for use herein include toluene, hexane, cyclohexane, and the like, as well as mixtures of any two or more thereof.

**[0094]** Assemblies of the invention can optionally include a first conductive layer. Such a conductive layer can be applied on either face of the above-described assembly, i.e., on either the reinforced thermoplastic layer of the assembly, or on the non-reinforced layer of the assembly. Preferably,

the first conductive layer is electrically conductive. Suitable materials contemplated for use as the electrically conductive layer, when present, include copper or an alloy thereof, nickel or an alloy thereof, nickel plated copper, nickel alloy plated copper, rolled copper-invar-copper, aluminum, or a combination of any two or more thereof. Preferably, the electrically conductive layer is copper or an alloy thereof.

**[0095]** In certain embodiments, the electrically conductive layer can be converted into frequency circuitry. This can be accomplished employing standard methodology, i.e., the invention assembly provides the advantage that it can be subjected to conventional processing conditions for the preparation of circuitry thereon.

**[0096]** In certain embodiments, inventive assemblies can further comprise a second conductive layer, wherein the second conductive layer can optionally be electrically conductive. The second electrically conductive layer may be formed into a second frequency dependent circuit element, or it may be left intact to define a ground plane. This can be prepared employing standard techniques known in the art.

**[0097]** Suitable materials contemplated for use as the second conductive layer include copper or an alloy thereof, nickel or an alloy thereof, nickel plated copper, nickel alloy plated copper, rolled copper-invar-copper, aluminum, or a combination of any two or more thereof. Preferably, the second conductive layer is copper or an alloy thereof. In other embodiments, the second conductive layer can define a ground plane.

**[0098]** In certain embodiments of the present invention, inventive assemblies can be applied to a variety of substrates. As readily recognized by those of skill in the art, substrates suitable for use in the practice of the present invention can include, but are not limited to, polyesters, polyamides, polyolefins, polyphenylene oxides, conductive metals, and the like, as well as combinations of any two or more thereof. When conductive metal substrates are employed, such materials as silver, nickel, gold, cobalt, copper, aluminum, graphite, silver-coated graphite, nickel-coated graphite, alloys of such metals, and the like, are contemplated for use herein.

#### Methods for Preparing Laminate Structures

**[0099]** In accordance with another embodiment of the present invention, there are provided laminated sheets produced by layering and molding one or more layer(s) of reinforced thermoplastic-containing layer and/or one or more non-reinforced thermoplastic layer(s). Laminated sheets according to the invention have many particularly beneficial properties, such as, for example, low dielectric constant, low electrical loss tangent, a glass transition temperature which is approximately the same as the glass transition temperature of the hydrocarbyl thermoplastic resin employed to prepare the assembly from which the laminate is prepared, high thermal decomposition temperature, and the like. In a preferred embodiment, laminated sheets according to the present invention have a dielectric constant  $\leq 4.5$  nominal, electrical loss tangent  $\leq 0.02$ , and a glass transition temperature of at least 80° C.

**[0100]** In accordance with a further embodiment of the present invention, there are provided printed wiring boards produced by forming conductive patterns on the surface of the above-described laminated sheet(s).

**[0101]** In accordance with a still further embodiment of the present invention, there are provided methods of making

printed wiring boards, said methods comprising forming conductive patterns on the surface of a laminated sheet according to the invention.

**[0102]** In accordance with yet another embodiment of the present invention, there are provided multilayer printed wiring boards produced by layering and molding a prescribed number of reinforced thermoplastic-containing layer(s) and non-reinforced thermoplastic layer(s), to obtain a printed wiring board for an inner layer, and layering a prescribed number of reinforced thermoplastic-containing layer(s) and non-reinforced thermoplastic layer(s) on the resulting printed wiring board for an inner layer, to obtain conductive patterns on the surface.

**[0103]** In accordance with still another embodiment of the present invention, there are provided methods of making multilayer printed wiring board, said methods comprising layering and molding a prescribed number of reinforced thermoplastic-containing layer(s) and non-reinforced thermoplastic layer(s) according to the invention, to obtain a printed wiring board for an inner layer, and layering a prescribed number of reinforced thermoplastic-containing layer(s) and non-reinforced thermoplastic layer(s) on the printed wiring board for an inner layer which forms conductive patterns on the surface.

**[0104]** Thus, in accordance with another aspect of the present invention, there are provided methods for preparing laminate structures, comprising subjecting the above described assemblies to conditions suitable to cure the thermoset component of the reinforced thermoplastic-containing layer, thereby causing the thermoplastic components of the reinforced and non-reinforced layers to form a bond (e.g., a cohesive or adhesive bond) therebetween. Preferably, the lengths of the reinforced and non-reinforced thermoplastic-containing layers in the assembly are the same. Component layers can be subjected to sufficient pressure to produce assemblies with substantially no air entrapped between the layers thereof, and without substantially altering the thickness of the component layers. Optionally, the assembly can include a first conductive layer, and optionally can include a second conductive layer.

**[0105]** The reinforced thermoplastic-containing layer of the laminate can include a porous substrate impregnated with a composition comprising: a first component comprising a low loss, low dielectric constant, hydrocarbyl thermoplastic resin; a second component which is capable of crosslinking to produce a thermoset in the presence of the first component; and a free radical source. Optionally, the first reinforced thermoplastic-containing layer can include one or more additives and/or a diluent. In preferred embodiments of the laminate, the resulting impregnated substrate is subjected to conditions suitable to remove substantially all of any diluent therein. Optionally, the laminate can include one or more conductive layers.

**[0106]** Preferably, the conditions to which the assembly are subjected include heating the assembly to a temperature sufficient to cause the thermoplastic polymer of the reinforced layer to flow. Preferably, the assembly is heated to a temperature greater than the melt transition temperature of the thermoplastic polymer of the reinforced layer, but not greater than the melt transition temperature of the thermoplastic polymer included in the non-reinforced layer, preferably to a temperature sufficient to cause the thermoplastic polymer of the reinforced layer to melt and sufficient to soften, but not melt, the thermoplastic polymer of the

non-reinforced layer, thus permitting molecular miscibility of the non-reinforced layer. Thus, the thermoplastic polymer of the reinforced layer can flow, while the thermoplastic polymer of the non-reinforced layer retains its shape while allowing permeation by the thermoplastic polymer of the reinforced layer. After maintaining the assembly at a desired temperature for a time sufficient to allow interaction between the thermoplastic polymers of the reinforced and non-reinforced layers, the assembly may be heated to a temperature sufficient to cure the thermoset resin.

[0107] The thermoplastic layers may optionally include additives and/or fillers, and may be produced by any suitable means, (e.g., slot extrusion, blown-film extrusion, sheet casting or the like).

[0108] Resulting laminate structures may include a first conductive layer, which can be further processed to create circuitry on the first conductive layer. In certain embodiments, the circuitry can be frequency dependent. In certain preferred embodiments, the frequency dependent circuitry can define a high frequency or digital device (e.g., a microwave antenna). Alternatively, a plurality of circuits can be created on the first conductive layer.

[0109] Resulting laminate structures may also include a second conductive layer, which can be further processed to create a second frequency dependent circuit element, or it may be left intact to define a ground plane. Optionally, resulting laminate structures which also include a second conductive layer, can be further processed to create circuitry on the first conductive layer of the assembly and a ground plane on the second conductive layer of the assembly.

[0110] Following formation of a bond (e.g., a cohesive or adhesive bond) between the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic-containing layer, the resulting laminate structure can be cut to the desired size and/or shape. In certain embodiments, the resulting laminate can be applied to a suitable substrate.

[0111] Assemblies of the present invention are preferably resistant to attack by acidic aqueous media, basic aqueous media and/or organic media, making it possible to subject such assemblies to a variety of processing conditions commonly used in PCB manufacturing, such as, for example, chemical etching to introduce circuitry thereto.

[0112] As readily recognized by those of skill in the art, invention assemblies can be applied to any of a variety of substrates for use. For example, circuits produced employing invention assemblies can be mounted on support structures, such as aluminum or composite materials intended as stiffeners, or the like, or can be combined with covers that act as protection from weather, for instance.

[0113] In certain embodiments, there are provided multi-layer assemblies comprising a plurality of the above-described assemblies of the invention. As readily recognized by those of skill in the art, a "plurality" of assemblies embraces stacking 2 up to greater than about 20 assemblies to produce complex interconnected circuitry. Optionally, such stacked assemblies may be internally interconnected by one or more through-holes.

[0114] In certain embodiments of the present invention, the assembly may be a thermoset laminate coated with a thermoplastic varnish compound. The thermoplastic varnish compound includes a thermosetting resin (preferably a low loss thermosetting resin) and a thermoplastic resin. The varnish optionally includes additives and fillers. Preferably, the major component in the thermoplastic varnish is a thermoplastic resin. The thermoplastic resin included in the thermoplastic varnish preferably has a melt solubility compatible with that of the thermoplastic material included in

the reinforced and non-reinforced thermoplastic layers. Additionally, it is preferred that the thermoplastic component of the varnish has lower melt and glass transition temperature than that of the reinforced and non-reinforced thermoplastic layers.

[0115] The invention will now be described in greater detail by reference to the following non-limiting examples.

#### EXAMPLE 1

[0116] An 80:20 solution of Topas 5013 cyclic-olefin copolymer (Topas Advanced Polymers) and Triallyl Isocyanurate (TAIC) in toluene was blended with 50 parts fused silica ceramic powder and a dicumyl peroxide initiator. This varnish was then coated to 80% resin content on 106 style woven fiberglass. The b-stage prepreg produced was then laminated (280° F. (138° C.) for 10 minutes and then 365° F. (185° C.) for 90 minutes at 250 PSI) in a vacuum press together with copper foil cladding of ½ oz. weight. Properties of the construction were evaluated and are summarized in Table 1.

TABLE 1

Property	Result	Unit
Dielectric Constant, Er	2.847	X-Band
Loss Tangent	0.0021	X-Band
Peel Strength, cladding	7.2	Lb/L.I.

[0117] The results presented in Table 1 reflect typical performance properties of a laminate according to the prior art comprising foil cladding on a thermoplastic-containing fiber reinforced substrate.

#### EXAMPLE 2

[0118] Topas 6017 grade cyclic-olefin copolymer (Topas Advanced Polymers) was extruded into approximately 0.020" sheets. Dielectric Constant and Loss Tangent of this sample were evaluated in the X-Band frequency range. Results are summarized in Table 2.

TABLE 2

Property	Result	Unit
Dielectric Constant, Er	2.315	X-Band
Loss Tangent	0.00087	X-Band

[0119] The results presented in Table 2 reflect typical performance properties of a non-reinforced thermoplastic film material.

#### EXAMPLE 3

[0120] Two sheets of ~0.020" extruded Topas 6017 grade cyclic-olefin copolymer were laminated (365° F. (185° C.), 60 minutes, 360 PSI) in a lab press with ½ oz. copper foil cladding. The extruded sheets fused together by way of cohesion while the foil cladding weakly bonded by adhesion. Performance properties of the resulting articles are summarized in Table 3.

TABLE 3

Property	Result	Unit
Peel Strength, cladding	2.0	Lb/L.I.
Peel Strength, internal	Fused, not feasible	Lb/L.I.

[0121] The results presented in Table 3 reflect typical bond strength of a laminate comprising foil cladding on thermoplastic film substrate.



## EXAMPLE 4

[0122] Constructions were pressed in a production scale press and were composed of two plies of the prepreg described in EXAMPLE 1 (at ~0.0036" each) sandwiched around a ~0.024" sheet of the extruded Topas 6017 sheet described in EXAMPLE 2 for a laminated thickness of

0.031". Constructions were clad with ½ oz. copper foil. Product was held at 280° F. (138° C.) for 15 minutes and then cured at 380° F. (193° C.) for 60 minutes at 360 PSI. Properties of the construction were evaluated and are summarized in Table 4.

TABLE 4

Property	Result	Unit
Dielectric Constant, Er	2.428	X-Band
Loss Tangent	0.00102	X-Band
Peel Strength, cladding	7.5	Lb/L.I.

[0123] The results presented in Table 4 demonstrate the superior performance properties achievable with invention laminates comprising foil cladding on a combination of a reinforced thermoplastic-containing layer and a non-reinforced thermoplastic layer.

## EXAMPLE 5

[0124] Constructions were pressed in a production scale press and were composed of ten plies of the prepreg described in EXAMPLE 1 (at ~0.0036" each) interleaved with nine plies of 0.003" film of the extruded Topas 6017 resin described in EXAMPLE 2, for a laminated thickness of 0.063". Product was held at 320° F. (160° C.) for 20 minutes and then cured at 365° F. (185° C.) for 60 minutes at 150 PSI. Properties of the construction were evaluated and are summarized in Table 5.

TABLE 5

Property	Result	Unit
Dielectric Constant, Er	2.594	X-Band
Loss Tangent	0.00159	X-Band
Peel Strength, cladding	7.2	Lb/L.I.

[0125] The results presented in Table 5 demonstrate the ability of invention methods to be employed for the preparation of multiple layer laminates, as well as the superior performance properties of the resulting laminates compris-

ing foil cladding on a combination of a reinforced thermoplastic-containing layer and a non-reinforced thermoplastic layer.

## EXAMPLE 6

[0126] The performance properties of the materials described in Examples 1, 2, 4 and 5 are compared in Table 6.

TABLE 6

Property	Unit	Prior Art Laminate (Example 1)	Thermoplastic film (Example 2)	Invention assembly (Example 4)	Invention assembly (Example 5)
Dielectric Constant, Er	X-Band	2.847	2.315	2.428	2.594
Loss Tangent	X-Band	0.0021	0.00087	0.00102	0.00159
Peel Strength, cladding	Lb/L.I.	7.2	2.0	7.5	7.2

[0127] The data presented in Table 6 demonstrate the superior performance properties of invention assemblies comprising foil cladding on a combination of a reinforced thermoplastic-containing layer and a non-reinforced thermoplastic layer. Specifically, invention assemblies display optimal low loss, peel performance and dielectric constant.

[0128] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0129] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising," "including," "containing," etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

[0130] Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification, improvement and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications, improvements and variations are considered to be within the scope of this invention. The materials, methods, and examples provided here are representative of preferred embodiments, are exemplary, and are not intended as limitations on the scope of the invention.

[0131] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0132] All publications, patent applications, patents, and other references mentioned herein are expressly incorporated by reference in their entirety, including all formulas and figures, to the same extent as if each were incorporated by reference individually. In case of conflict, the present specification, including definitions, will control.

[0133] Other embodiments are set forth within the following claims.

That which is claimed is:

1. An assembly comprising:

a first reinforced thermoplastic-containing layer, and  
a first non-reinforced thermoplastic layer,

wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of interacting sufficiently so as to form a bond therebetween,

wherein said first reinforced thermoplastic-containing layer comprises a porous substrate impregnated with a composition comprising:

- (a) a first component comprising a low loss, low dielectric constant, hydrocarbyl thermoplastic resin,
- (b) a second component which is capable of crosslinking to produce a thermoset in the presence of the first component,
- (c) a free radical source,
- (d) optionally, one or more additives, and
- (e) an optional diluent therefore,

wherein the resulting impregnated substrate has been subjected, if necessary, to conditions suitable to remove substantially all of the optionally present diluent therefrom.

2. An assembly according to claim 1 wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer have compatible melt solubility.

3. An assembly according to claim 1 wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of forming an adhesive bond therebetween.

4. An assembly according to claim 1 wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of forming a mechanical bond therebetween.

5. An assembly according to claim 1 wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer interact sufficiently to produce an interlayer peel strength of at least about four pounds per linear inch.

6. An assembly according to claim 1 wherein said porous substrate is woven or non-woven.

7. An assembly according to claim 1 wherein said porous substrate is selected from the group consisting of woven glass, non-woven glass, woven aramid fibers, non-woven aramid fibers, woven liquid crystal polymer fibers, non-woven liquid crystal polymer fibers, woven synthetic polymer fibers, non-woven synthetic polymer fibers, randomly dispersed fiber reinforcements, expanded PTFE structures and combinations of any two or more thereof.

8. An assembly according to claim 1 wherein said porous substrate is selected from the group consisting of fiberglass, quartz, polyester fiber, polyamide fiber, polyphenylene sulfide fiber, polyetherimide fiber, cyclic olefin copolymer fiber, polyalkylene fiber, liquid crystalline polymer, poly(p-phenylene-2,6-benzobisoxazole), and mixtures of any two or more thereof.

9. An assembly according to claim 1 wherein said porous substrate is of glass formulation types E, S, C, or D.

10. An assembly according to claim 1 wherein said porous substrate is selected from the group consisting of aramid fiber, polytetrafluoroethylene, a copolymer of tetrafluoroethylene and perfluoromethylvinyl ether (MFA).

11. An assembly according to claim 1, further comprising one or more additional reinforced thermoplastic-containing layer(s).

12. An assembly according to claim 1 wherein said first non-reinforced thermoplastic layer has a thickness of at least about 10 microns.

13. An assembly according to claim 1 wherein said non-reinforced thermoplastic layer comprises a thermoplastic resin selected from the group consisting of cyclic olefin copolymer, terpolymers, block copolymers, or combinations of any two or more thereof.

14. An assembly according to claim 13 wherein said non-reinforced thermoplastic resin is selected from the group consisting of cyclic olefin copolymers, polyetherimides, polyether ether ketones (PEEKs), liquid crystal polymers (LCPs), polytetrafluoroethylene, polyphenylenesulfide, polyphenyleneoxide, polyphenylene ether, polymethylpentene (TPX), polypropylene, and polyethylene.

15. An assembly according to claim 1 wherein said non-reinforced thermoplastic layer contains one or more inorganic or organic fillers.

16. An assembly according to claim 1 wherein said filler is selected from the group consisting of ceramics, fused silica, glass bubbles, glass spheres, glass powder, polymeric spheres, polymeric bubbles, aluminum nitride, boron nitride, silicon carbide, diamond, graphite, beryllium oxide, magnesia, silica, titanium oxide, strontium oxide, perfluorinated hydrocarbon polymers, thermoplastic polymers, thermoplastic elastomers, mica, aluminum oxide, cordierite, stearite, barium titanate, magnesium titanate, and neodymium titanate.

17. An assembly according to claim 1 wherein said non-reinforced thermoplastic layer contains one or more inorganic or organic micro-fibers selected from the group consisting of glass, quartz, aramid, carbon fiber, and polytetrafluoroethylene.

18. An assembly according to claim 11, further comprising one or more additional non-reinforced thermoplastic layer(s).

19. An assembly according to claim 1 further comprising a first conductive layer.

20. An assembly according to claim 19 wherein said first conductive layer is electrically conductive.

21. An assembly according to claim 20 wherein said first electrically conductive layer is copper or an alloy thereof, nickel or an alloy thereof, nickel or nickel alloy plated copper, rolled copper-invar-copper, aluminum, or a combination of any two or more thereof.

22. An assembly according to claim 20 wherein said first electrically conductive layer is copper or an alloy thereof.

23. An assembly according to claim 20 wherein said first electrically conductive layer is capable of being converted into frequency dependent circuitry.

24. An assembly according to claim 19, further comprising a second conductive layer.

25. An assembly according to claim 24 wherein said second conductive layer is electrically conductive.

26. An assembly according to claim 25 wherein said second electrically conductive layer is copper or an alloy thereof, nickel or an alloy thereof, nickel or nickel alloy plated copper, rolled copper-invar-copper, aluminum, or a combination of any two or more thereof.

27. An assembly according to claim 25 wherein said second electrically conductive layer is copper or an alloy thereof.

28. An assembly according to claim 24 wherein said second conductive layer defines a ground plane.

29. An assembly according to claim 1 wherein the assembly has a dielectric constant of between about 2.0 to about 4.5.

30. A laminate comprising:  
a first reinforced thermoplastic-containing layer, and  
a first non-reinforced thermoplastic layer,  
wherein the reinforced thermoplastic-containing layer and the non-reinforced thermoplastic layer are capable of interacting sufficiently so as to form a bond therebetween,  
wherein said first reinforced thermoplastic-containing layer comprises a porous substrate impregnated with a composition comprising:  
(a) a first component comprising a low loss, low dielectric constant, hydrocarbyl thermoplastic resin,  
(b) a second component which is capable of crosslinking to produce a thermoset in the presence of the first component,  
(c) a free radical source,  
(d) optionally, one or more additives, and  
(e) an optional diluent therefore,

wherein the resulting impregnated substrate has been subjected, if necessary, to conditions suitable to remove substantially all of the optionally present diluent therefrom.

31. A laminate according to claim 30 further comprising a first conductive layer.

32. A laminate according to claim 31 further comprising a second conductive layer.

33. A method for preparing a laminate according to claim 30, said method further comprising subjecting a stack comprising said first reinforced thermoplastic-containing layer and said first non-reinforced thermoplastic layer to conditions suitable to cure the thermoset component of said reinforced thermoplastic-containing layer, and cause the thermoplastic component of said reinforced thermoplastic-containing layer and said non-reinforced thermoplastic layer to form a bond therebetween.

34. A method according to claim 33 wherein said conditions are sufficient to cause the thermoplastic component of said reinforced thermoplastic-containing layer to flow and said non-reinforced thermoplastic layer to soften sufficiently

so as to permit molecular miscibility between each of the layers sufficient to form said bond therebetween.

35. A method according to claim 33 wherein each of said layers are provided in continuous lengths.

36. A method according to claim 35 wherein the resulting assembly is thereafter cut into the desired size and/or shape.

37. A method for preparing a laminate according to claim 31, said method comprising subjecting a stack comprising said first conductive layer, said first reinforced thermoplastic-containing layer, and said first non-reinforced thermoplastic layer to conditions suitable to cure the thermoset component of said reinforced thermoplastic-containing layer, and cause the thermoplastic component of said reinforced thermoplastic-containing layer and said non-reinforced thermoplastic layer to form a bond therebetween.

38. A method for preparing a laminate according to claim 32, said method comprising subjecting a stack comprising said first conductive layer, said first reinforced thermoplastic-containing layer, said first non-reinforced thermoplastic layer, a second reinforced thermoplastic-containing layer, and said second conductive layer to conditions suitable to cure the thermoset component of said reinforced thermoplastic-containing layer, and cause the thermoplastic component of said reinforced thermoplastic-containing layers and said non-reinforced thermoplastic layer(s) to form a bond therebetween.

39. A method for preparing an article useful for the formation of frequency dependent circuitry, said method comprising subjecting an assembly according to claim 24 to processing suitable to create circuitry on the first conductive layer and/or a ground plane on the second conductive layer of said assembly.

40. A method according to claim 39 wherein said the resulting article containing frequency dependent circuitry defines a high frequency or digital device.

41. A method according to claim 39 wherein a plurality of circuits are created on the first conductive layer.

42. A method according to claim 39 further comprising a plurality of circuits applied to said first conductive layer.

43. A method according to claim 39 further comprising applying the resulting assembly to a suitable substrate.

44. A method for preparing an article useful for the formation of frequency dependent circuitry, said method comprising subjecting a laminate according to claim 32 to processing suitable to create circuitry on the first conductive layer and/or a ground plane on the second conductive layer of said laminate.

45. A stacked assembly comprising a plurality of assemblies according to claim 1.

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