EXPANDED AND EXPANDABLE HIGH GLASS TRANSITION TEMPERATURE POLYMERS

BACKGROUND OF INVENTION

This disclosure relates to expandable and expandable polymeric materials. In particular, the disclosure relates to expandable and expanded materials comprising a high glass transition temperature thermoplastic.

Expanded thermoplastic materials, also known as thermoplastic foams, are thermoplastic materials which comprise voids (also known as pores or cells) that reduce the density of the material when compared to a comparable unexpanded thermoplastic material. The thermoplastic foam may further comprise a filler such as a particulate filler or a fibrous filler. The expanded thermoplastic material may be compressible or rigid, depending on the application. Expandable materials are thermoplastic materials that, when subjected to the required conditions, expand to form an expanded composition.

Expanded thermoplastic materials have a wide range of uses including impact absorption, sound insulation, temperature insulation, structural applications, and the like. In some cases, such as aerospace, submarine, high speed trains, and applications such as thermal imaging there is a need for foams having flame retardancy, heat resistance, and thermal stability over a wide range of temperatures. In some cases, mechanical strength is also required. Expanded materials may be optionally combined with other materials, such as films or sheets, depending on the characteristics required in the final application.

Polyimide foams, as taught in EP 0373402, U.S. Patent Nos. 4,543,368, 4,683,247, 4,980,389, 5,064,867, 5,135,959, 5,234,966 and 6,057,379 have addressed some of these needs but as foams are employed in increasingly rigorous conditions there is an ongoing need for foams comprising high glass transition temperature polymers.

SUMMARY OF THE INVENTION

The present invention is directed to an expandable or expanded composition, such as a foam, comprising either: a) an immiscible blend of polymers comprising one or more polyetherimides, having more than one glass transition temperature wherein the polyetherimide has a glass transition temperature greater than 217° Celsius; b) a miscible blend of polymers, comprising one or more polyetherimides, having a single glass transition temperature greater than 180° Celsius; or, c) a single polyetherimide having a glass transition temperature of greater than 247° Celsius.

The expandable composition may further comprise a blowing agent.

DETAILED DESCRIPTION OF THE INVENTION

As used herein the term "hydrogen atom to carbon atom numerical ratio" is the ratio of the number of hydrogen atoms to the number of carbon atoms in the polymer or the repeat unit (monomer) making up the polymer.

The definition of benzylic proton is well known in the art, and in terms of the present invention it encompasses at least one aliphatic carbon atom chemically bonded directly to at least one aromatic ring, such as a phenyl or benzene ring, wherein said aliphatic carbon atom additionally has at least one proton directly bonded to it.

In the present context substantially or essentially free of benzylic protons means that the polymer, such as for example the polyimide sulfone product, has less than about 5 mole % of structural units, in some embodiments less than about 3 mole % structural units, and in other embodiments less than about 1 mole % structural units derived containing benzylic protons. Free of benzylic protons, which are also known as benzylic hydrogens, means that the polyetherimide article zero mole % of structural units derived from monomers and end cappers containing benzylic protons or benzylic hydrogens. The amount of benzylic protons can be determined by ordinary chemical analysis based on the chemical structure.

The expanded thermoplastic composition described herein has excellent heat stability and flame retardance making it useful in a range of applications where heat stability is particularly valuable.

The present invention is directed to an expandable or expanded composition, such as a foam, comprising either: a) an immiscible blend of polymers comprising one or more polyetherimides, having more than one glass transition temperature wherein the polyetherimide has a glass transition temperature greater than 217° Celsius; b) a miscible blend of polymers, comprising one or more polyetherimides, having a single glass transition temperature greater than 180° Celsius; or, c) a single polyetherimide having a glass transition temperature of greater than 247° Celsius.

In some embodiments the expanded composition has a bulk density of 20 to 200 kilograms per cubic meter (kg/m^3) plus or minus 10%. Within this range the bulk density may be less than or equal to 90 kg/m^3, or more specifically, less than or equal to 75 kg/m^3 or less than or equal to 50 kg/m^3, or less than or equal to 40, 35, 30, 25 and 20 kg/m. Also within this range the bulk density is substantially uniform through the material.

The expanded thermoplastic composition may have an open cell or closed cell structure. Additionally, the expanded thermoplastic composition may be flexible or rigid.

Foams according to the present invention may also transmit radar waves. In this regard, foams according to the present invention may be transparent, ie allowing substantially all of the radar waves hitting the polymer to be transmitted through the polymer; translucent, ie transmitting between 40 and 95% of the radar waves hitting the polymer, or opaque, ie transmitting less than 40% of the radar waves hitting the polymer.

The foams according to the present invention may have a dielectric constant of between about .75 to about 2.00, or between 1.00 and 1.50 or between 1.05 and 1.11.

The expanded thermoplastic composition may comprise one or more fillers. In some cases fillers function as nucleating agents and help to stabilize the formation of pores during expansion. Exemplary fillers include silica powder, such as fused silica and crystalline silica; boron-nitride powder and boron-silicate powders; alumina, and magnesium oxide (or magnesia); wollastonite including surface-treated wollastonite; calcium sulfate (as its anhydride, dihydrate or trihydrate); calcium carbonate including chalk, limestone, marble and synthetic, precipitated calcium carbonates, generally in the form of a ground particulates; talc, including fibrous, modular, needle shaped, and lamellar talc; glass spheres, both hollow and solid; kaolin, including hard, soft, calcined kaolin, and kaolin comprising various coatings known in the art to facilitate compatibility with the polymeric matrix resin; mica; feldspar; silicate spheres; flue dust; cenospheres; fillite; aluminosilicate (armospheres); natural silica sand; quartz; quartzite; perlite; tripoli; diatomaceous earth; synthetic silica; and combinations thereof. All of the above fillers may be surface treated with silanes to improve adhesion and dispersion with the polymeric matrix resin.

Additional exemplary reinforcing fillers include flaked fillers that offer reinforcement such as glass flakes, flaked silicon carbide, aluminum diboride, aluminum flakes, and steel flakes. Exemplary reinforcing fillers also include fibrous fillers such as short inorganic fibers, natural fibrous fillers, single crystal fibers, glass fibers, and organic reinforcing fibrous fillers. Short inorganic fibers include those derived from blends comprising at least one of aluminum silicates, aluminum oxides, magnesium oxides, and calcium sulfate hemihydrate. Natural fibrous fillers include wood flour obtained by pulverizing wood, and fibrous products such as cellulose, cotton, sisal, jute, starch, cork flour, lignin, ground nut shells, corn, rice grain husks. Single crystal fibers or "whiskers" include silicon carbide, alumina, boron carbide, iron, nickel, and copper single crystal fibers. Glass fibers, including textile glass fibers such as E, A, C, ECR, R, S, D, and NE glasses and quartz, and the like may also be used. In addition, organic reinforcing fibrous fillers may also be used including organic polymers capable of forming fibers. Illustrative examples of such organic fibrous fillers include, for example, poly(ether ketone), polyimide, polybenzoxazole, poly(phenylene sulfide), polyesters, polyethylene, aromatic polyamides, aromatic

polyimides or polyetherimides, polytetrafluoroethylene, acrylic resins, and poly(vinyl alcohol). Such reinforcing fillers may be provided in the form of monofilament or multifilament fibers and can be used either alone or in combination with other types of fiber, through, for example, co-weaving or core/sheath, side-by-side, orange-type or matrix and fibril constructions, or by other methods known to one skilled in the art of fiber manufacture. Typical cowoven structures include glass fiber-carbon fiber, carbon fiber-aromatic polyimide (aramid) fiber, and aromatic polyimide fiber-glass fiber. Fibrous fillers may be supplied in the form of, for example, rovings, woven fibrous reinforcements, such as 0-90 degree fabrics, non-woven fibrous reinforcements such as continuous strand mat, chopped strand mat, tissues, papers and felts and 3-dimensionally woven reinforcements, performs and braids.

The optional electrically conductive additive may comprise electrically conductive carbon black, carbon nanotubes, carbon fibers or a combination of two or ore of the foregoing. Electrically conductive carbon blacks are commercially available and are sold under a variety of trade names, including but not limited to S.C.F. (Super Conductive Furnace), E.C.F. (Electric Conductive Furnace), Ketjen Black EC (available from Akzo Co., Ltd.) or acetylene black. In some embodiments the electrically conductive carbon black has an average particle size less than or equal to 200 nanometers (nm), or, more specifically, less than or equal to 100 nm, or, even more specifically, less than or equal to 50 nm. The electrically conductive carbon blacks may also have surface areas greater than 200 square meter per gram (m^2/g), or, more specifically, greater than 400 m^2/g, or, even more specifically, greater than 1000 m^2/g. The electrically conductive carbon black may have a pore volume greater than or equal to 40 cubic centimeters per hundred grams ($cm^3/100g$), or, more specifically, greater than or equal to 100 $cm^3/100g$, or, even more specifically, greater than or equal to 150 $cm^3/100g$, as determined by dibutyl phthalate absorption.

Carbon nanotubes that can be used include single wall carbon nanotubes (SWNTs), multiwall carbon nanotubes (MWNTs), vapor grown carbon fibers (VGCF) and combinations comprising two or more of the foregoing. Carbon nanotubes can also be considered to be reinforcing filler.

Single wall carbon nanotubes (SWNTs) may be produced by laser-evaporation of graphite, carbon arc synthesis or a high-pressure carbon monoxide conversion process (HIPCO) process. These SWNTs generally have a single wall comprising a graphene sheet with outer diameters of 0.7 to 2.4 nanometers (nm). The SWNTs may comprise a mixture of metallic SWNTs and semi-conducting SWNTs. Metallic SWNTs are those that display electrical characteristics similar to metals, while the semi-conducting SWNTs are those that are electrically semi-conducting. In some embodiments it is desirable to have the composition comprise as large a fraction of metallic SWNTs as possible. SWNTs may have aspect ratios of greater than or equal to 5, or, more specifically, greater than or equal to 100, or, even more specifically, greater than or equal to 1000. While the SWNTs are generally closed structures having hemispherical caps at each end of the respective tubes, it is envisioned that SWNTs having a single open end or both open ends may also be used. The SWNTs generally comprise a central portion, which is hollow, but may be filled with amorphous carbon.

In one embodiment the SWNTs comprise metallic nanotubes in an amount of greater than or equal to 1 wt%, or, more specifically, greater than or equal to 20 wt%, or, more specifically, greater than or equal to 30 wt%, or, even more specifically greater than or equal to 50 wt%, or, even more specifically, greater than or equal to 99.9 wt% of the total weight of the SWNTs.

In one embodiment the SWNTs comprise semi-conducting nanotubes in an amount of greater than or equal to 1 wt%, or, more specifically, greater than or equal to 20 wt%, or, more specifically, greater than or equal to 30 wt%, or, even more specifically, greater than or equal to 50 wt%, or, even more specifically, greater than or equal to 99.9 wt% of the total weight of the SWNTs.

MWNTs may be produced by processes such as laser ablation and carbon arc synthesis. MWNTs have at least two graphene layers bound around an inner hollow core. Hemispherical caps generally close both ends of the MWNTs, but it is also possible to use MWNTs having only one hemispherical cap or MWNTs which are devoid of both caps. MWNTs generally have diameters of 2 to 50 nm. Within this

range, the MWNTs may have an average diameter less than or equal to 40, or, more specifically, less than or equal to 30, or, even more specifically less than or equal to 20 nm. MWNTs may have an average aspect ratio greater than or equal to 5, or, more specifically, greater than or equal to 100, or, even more specifically greater than or equal to 1000.

Vapor grown carbon fibers (VGCF) are generally manufactured in a chemical vapor deposition process. VGCF having "tree-ring" or "fishbone" structures may be grown from hydrocarbons in the vapor phase, in the presence of particulate metal catalysts at moderate temperatures, i.e., 800 to 1500°C. In the "tree-ring" structure a multiplicity of substantially graphitic sheets are coaxially arranged about the core. In the "fishbone" structure, the fibers are characterized by graphite layers extending from the axis of the hollow core.

VGCF having diameters of 3.5 to 2000 nanometers (nm) and aspect ratios greater than or equal to 5 may be used. VGCF may have diameters of 3.5 to 500 nm, or, more specifically 3.5 to 100 nm, or, even more specifically 3.5 to 50 nm. VGCF may have an average aspect ratios greater than or equal to 100, or, more specifically, greater than or equal to 1000.

Various types of conductive carbon fibers may also be used in the composition. Carbon fibers are generally classified according to their diameter, morphology, and degree of graphitization (morphology and degree of graphitization being interrelated). These characteristics are presently determined by the method used to synthesize the carbon fiber. For example, carbon fibers having diameters down to 5 micrometers, and graphene ribbons parallel to the fiber axis (in radial, planar, or circumferential arrangements) are produced commercially by pyrolysis of organic precursors in fibrous form, including phenolics, polyacrylonitrile (PAN), or pitch.

The carbon fibers generally have a diameter of greater than or equal to 1,000 nanometers (1 micrometer) to 30 micrometers. Within this range fibers having sizes of greater than or equal to 2, or, more specifically, greater than or equal to 3, or, more specifically greater than or equal to 4 micrometers may be used. Also within this

range fibers having diameters of less than or equal to 25, or, more specifically, less than or equal to 15, or, even more specifically less than or equal to 11 micrometers may be used.

The expanded thermoplastic composition results from the expansion (or foaming) of an expandable thermoplastic composition. Expandable thermoplastic compositions may be produced in a number of ways. In a first embodiment a composition comprising a polymer precursor or combination of polymer precursors is subjected to microwave energy, heat or a combination of microwave energy and heat to foam the composition. The polymer precursors are oligomers, which, when subjected to microwave energy, heat and/or further polymerize. The further polymerization produces byproduct(s) which can be is volatile at the temperature and pressure under which the further polymerization occurs. The byproduct acts as the foaming (or blowing) agent. The foamed composition may then be subjected to further heat for further polymerization, for example at 200-500°C for 0.5 to 4 hours.

Exemplary polymeric precursors may be produced by reacting a dianhydride with an alcohol to form an ester. The dianhydride and alcohol may be reacted in a suitable solvent. In one embodiment the alcohol is used as a solvent. Exemplary alcohols include aliphatic alcohols having 1 to 7 carbon atoms and aromatic alcohols. Typically, a slight excess of alcohol beyond the quantity required to dissolve the dianhydride produces best results. The reaction is carried out at elevated temperatures, for example temperatures above the boiling point of the solvent. The ester is then reacted with a polyamine such as a diamine to form a polymeric precursor. The optional filler can be blended into the solution at this point. The solvent may be removed to thicken or dry the precursor. Typically, spray drying, vacuum drying or heating at a temperature of 50° to 90° C may be used. In one embodiment the optional filler is dry blended with the dried precursor.

In one embodiment a solution or slurry comprising the polymeric precursor, optional filler and at least one polar protic foam-enhancing additive is used for foaming. The protic foam-enhancing additive has the formula ROH, where R is hydrogen, or a C_1 to C_{12} linear or branched alkyl or cycloalkyl radical, which may be unsubstituted or

substituted with halo, aryl, alkoxy and hydroxy. The polar protic foam-enhancing additive need not be miscible with polymeric precursor or act as a solvent for any of the components of the composition under ambient, i.e. room temperature, conditions. Use of polar protic foam-enhancing additives is disclosed in U.S. Patent No. 5,234,966.

The composition comprising a polymer precursor may be preheated to a temperature below the foaming temperature for a time sufficient to obtain a substantially even temperature throughout the composition prior to increasing the temperature for foaming. In one embodiment the composition comprising a polymeric precursor is subjected to bulk reduction prior to foaming.

In an exemplary embodiment the composition comprising a polymeric precursor is pre-heated for 1 to 30 minutes at 120° C. to 180° C. in a convection oven. The pre-heating temperature is chosen to be high enough to obtain the fluidity of the precursor and low enough so that the precursor particles don't melt, both of which are important for a homogeneous cell structure.

When the expanded composition comprises an immiscible blend the two polymeric phases may be co-continuous or one polymeric phase may be dispersed in the other polymeric phase. In embodiments where the expanded composition is produced through the use of polymeric precursors, the polymeric precursors may be for one or both of the polymeric phases. In embodiments where the polymeric precursor is for only one of the polymeric phases the polymeric precursor can be blended with the second polymer prior to expansion.

When the expanded composition comprises a miscible blend of two polymers, one or both of the polymers may be produced through the use of polymeric precursors as discussed above.

An alternative approach to making an expanded polymeric composition comprises combining the polymeric composition with a blowing agent. Suitable blowing agents are described, for example, in U.S. Patent 4,543,368, herein incorporated by reference in its entirety. Blowing agents can include chemical blowing agents and/or physical

blowing agents. Chemical blowing agents are chemical compounds that decompose with a high gas yield under specified conditions, for example within a narrow temperature range. The decomposition products formed during the decomposition process are preferably physiologically safe, and do not significantly adversely effect the thermal stability or mechanical properties of the foamed polyurethane sheets. In addition, it is preferred that the decomposition products not effloresce or have a discoloring effect on the foam product.

In another aspect, the blowing agent is soluble in the resin at room temperature as well as at the processing temperature of the incorporation step and thereafter comes out of solution during an expanding step conducted at or nearly at the glass transition temperature of the imbibed resin. In one such method, the blowing agent is incorporated into the resin by exposing the resin to a saturated atmosphere of the blowing agent at a temperature below the glass transition temperature of the resin (yet at which the blowing agent will dissolve into the resin) and at elevated pressure. In another such method, the resin is suspended in a mixture of blowing agent and inert carrier fluid at an elevated temperature but, again, at a temperature at which the blowing agent is sufficiently soluble in the resin.

One important consideration when selecting a blowing agent is that it must produce a vapor pressure sufficient to expand the polymer walls once the polymer has softened due to heating. Propellant selection in this regard will thus depend on the softening temperature of the polymer chosen to form the microsphere shell walls as well as the vapor pressure of the blowing agent at this softening temperature. Typically, a solvent that has a boiling point at atmospheric pressure of no more than 10 degrees above the softening temperature (or glass transition temperature, Tg) of the polymer will provide a sufficient vapor pressure to expand said polymer shell walls upon heating the polymer to the boiling point of the blowing agent. More preferably, the boiling point of the propellant liquid at atmospheric pressure will be equal to or less than the polymer Tg, and even more preferably, the propellant boiling point will be at least 10 degrees lower than the polymer Tg.

Particularly preferred liquid blowing agents are the small chain hydrocarbons since they are inert towards most polymers, miscible with most solvents, and have boiling points near ambient temperatures. For liquid blowing agents that have boiling points below ambient temperatures, the process may advantageously be carried out at low temperatures and/or under a pressurized atmosphere.

Examples of liquid propellants that may be used in conjunction with the polymers and solvents listed above include, but are not limited to, hydrocarbons (n-butane, iso-butane, n-pentane, iso-pentane, trimethyl-2-pentene, hexane, heptane, n-octane, iso-octane, nonane, decane, benzene, toluene, etc.), ethers and ketones (ethyl ether, isopropyl ether, acetone, methyl ethyl ketone, etc.), alcohols (methanol, ethanol, iso-propanol, etc.), halogentated hydrocarbons (methylene chloride, chloroform, carbon tetrachloride, dichloroethane, trichloroethane, tetrachloroethane, tetrachloroethylene, trichlorofluoromethane, dichlorodifluorodimethane, etc.), ammonia or ammonia-based liquids, silane or siloxane-based liquids (hexamethyl disilane, hexamethyl disiloxane), and water or other aqueous mixtures. These examples are not meant to be exhaustive, for one skilled in the art will know of many liquids which will exhibit miscibility with a given polymer-solvent mixture while also exhibiting incompatibility with the pure polymer, and at the same time exerting a vapor pressure sufficient to expand said polymer shell walls at or above the softening temperature of the polymer.

Physical blowing agents may also be used, alone or as mixtures with each other or with one or more chemical blowing agents. Physical blowing agents have a boiling point below the glass transition temperature of the resin/blowing agent mixture or resin blend/blowing agent mixture (both of which are described herein as "the imbibed resin"). The blowing agent should be relatively soluble in the resin or resin blend well below the glass transition temperature (T_g) of the imbibed resin (e.g. at room temperature of about 20° C), yet relatively insoluble at the T_g of the imbibed resin. Examples of physical blowing agents include esters, especially lower alkyl esters such as ethyl acetate, methyl acetate and isopropyl acetate, and halogenated counterparts of the same, as well as ketones, especially lower alkyl ketones such as acetone and methyl ethyl ketone as well as cyclohexanone, and halogenated

counterparts of the same. By "relatively soluble" we mean that the physical blowing agent is sufficiently soluble in the resin to provide an imbibed resin having dissolved therein a sufficient, effective amount of the physical blowing agent. By "relatively insoluble" we mean that a sufficient, effective amount of the physical blowing agent comes out of solution to expand the resin. Thus, the blowing agent can be dissolved into the resin or resin blend to produce a storage-stable imbibed resin (expandable composition). The blowing agent comes out of solution to blow the resin when the imbibed resin is heated to its T_g during a subsequent expanding step. The amount of blowing agent dissolved in the resin should be sufficient and effective to produce expansion (blowing) of the composition during the subsequent expanding step. The expandable resin compositions may be provided in the form of pellets or particles which are conveniently expanded and concurrently molded into a variety of useful articles.

Reference is made throughout to the glass transition temperature of the resin or resin blend/physical blowing agent mixture (i.e. "the imbibed resin"); this is because the addition of blowing agent may change (depress) the T_g of the resin.

As with the chemical blowing agents, the physical blowing agents are used in an amount sufficient to give the resultant foam the desired bulk density. Typically, physical blowing agents are used in an amount of about 5 to about 50% by weight of the composition.

Physical blowing agents are those which produce a vapor by changing phase upon heating. There are a vast number of chemicals that exist as a solid at room temperature, yet vaporize upon reaching temperatures typically used to soften most polymers. Some solid blowing agents of this type pass through an intermediate liquid state upon heating, while others sublime directly to a gas upon heating. Examples of suitable physical blowing agents include, but are not limited to: neopentyl alcohol, hexamethyl ethane, tertiary-butyl carbazate, tertiary-butyl dimethylsilyl chloride, tertiary-butyl N-allylcarbamate, and tetramethyl-1,3-cyclobutanedione, etc. This list is not meant to be exhaustive as one knowledgeable in the field of chemistry will find many substances that meet the criteria described above. In selecting a suitable

physical blowing agent, consideration may be given to toxicity, polymer compatibility, solvent compatibility, melting point, boiling point, vapor pressure, or other issues, depending on the particular polymer-solvent system under consideration.

Chemical blowing agents, typically solid at ambient pressure and temperature, undergo decomposition or other chemical reactions that produce gaseous vapors as at least one of the reaction by-products. These reactions are most often triggered by heat, but can alternatively be triggered by the presence of a co-reactant. For instance, a chemical blowing agent could be triggered by the presence of water, whereby water is included in the formulation but only becomes available for reaction upon the addition of heat. (Such would be the case for certain hydrated salt compounds mixed with the chemical blowing agent sodium borohydride.) Chemical propellants can be categorized as either organic or inorganic chemical blowing agents. Inorganic chemical blowing agents typically decompose to give off carbon dioxide gas in an endothermic reaction. Organic chemical blowing agents typically decompose to give off nitrogen gas (which has a lower diffusion rate in most polymers) in an exothermic reaction.

Examples of chemical blowing agents include, but are not limited to: sodium bicarbonate, potassium hydrogencarbonate, sodium borohydride (decomposes upon the addition of a proton donor such as water), polycarbonic acid, ammonium carbonate, ammonium carbamate, ammonium acetate, ammonium diethyldithiocarbamate, dinitrosopentamethylene-tetraamine, p-toluenesulfonyl hydrazide, 4,4'-oxybis(benzenesulfonyl hydrazide), azodicarbonamide, p-toluenesulfonyl semicarbazide, 5-phenyltetrazole, diazoaminobenzene, etc. One advantage of chemical blowing agents is that the carbon dioxide or nitrogen gas typically evolved is inert, nonflammable, and nontoxic. Another advantage is that the inorganic blowing agents can themselves be very inert and nontoxic, which makes them easy and safe to work with during production and in the end-use products.

Solid blowing agents, both physical and chemical (organic and inorganic), avoid the inherent hazards associated with volatile, flammable liquids. Another advantage to be realized by the solid propellants is that the temperature at which microsphere

expansion occurs may be altered independent of the polymer used to make the microsphere shell walls. In conventional microspheres, the temperature at which expansion occurs is determined by the softening temperature of the polymer. That is, expansion occurs when the polymer shell walls soften, allowing the vapor pressure of a volatile liquid to stretch the walls outward.

Using the solid propellants described above and in accordance with this invention, however, the polymer-propellant combination may be chosen so that the expansion temperature is dictated by the decomposition temperature of the solid propellant rather than the softening temperature of the polymer. This will occur when the softening temperature of the polymer is below the decomposition temperature of the propellant. As the microcapsules are heated the polymer may soften, but as long as no gas is generated, no expansion will occur. Only upon heating further, to the decomposition temperature of the propellant, will a vapor pressure sufficient to expand the polymer shell walls be generated. Thus, by using solid-phase blowing agents which exert virtually no vapor pressure prior to the onset of decomposition, the temperature at which microsphere expansion occurs may be controlled by the selection of the propellant rather than by the softening temperature of the polymer. This feature can provide added flexibility in designing the temperature ramp-up cycle during the molding processes used to produce final products.

Chemical blowing agents offer an additional advantage over physical blowing agents (liquid or solid) in that they are capable of generating a higher expansion pressure than their physical blowing agent counterparts. This is because physical blowing agents will always be in a state of reversible equilibrium between the liquid and vapor phases. In contrast, the chemical blowing agents decompose to form inert gases in an essentially irreversible process. Because the decomposition is virtually irreversible and the gases produced are difficult to condense, chemical blowing agents are capable of producing much greater pressures than those generated by even the most volatile physical blowing agents.

Solubility of the propellant in the polymer-solvent mixture, the amount of gas generated, the vapor pressure generated, and the temperature at which vapor

generation occurs are all parameters that will influence the selection of an appropriate solid propellant for use in accordance with this invention.

The chemical blowing agent is chosen with a consideration for the glass transition temperature or softening temperature of the polymer or polymer blend. Generally the chemical blowing agent decomposes at a temperature above the softening temperature or glass transition temperature of the polymer or polymer blend. Exemplary chemical blowing agents include azo compounds, for example, azoisobutyronitrile, azodicarbonamide (i.e. azo-bis-formamide) and barium azodicarboxylate; substituted hydrazines, for example, diphenylsulfone-3,3'-disulfohydrazide, 4,4'-hydroxy-bis-(benzenesulfohydrazide), trihydrazinotriazine or aryl-bis-(sulfohydrazide); semicarbazides, for example, p-tolylene sulfonyl semicarbazide or 4,4'-hydroxy-bis-(benzenesulfonyl semicarbazide); triazoles, for example, 5-morpholyl-1,2,3,4-thiatriazole; and N-nitroso compounds, for example, N,N'- dinitrosopentamethylene tetramine or N,N-dimethyl-N,N'- dinitrosophthalmide; benzoxazines, for example, isatoic anhydride; or mixtures such as, for example, sodium carbonate/citric acid mixtures, 5-phenyltetrazole, calcium oxalate, trihydrazino-s-triazine, 5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, and 3,6-dihydro-5,6-diphenyl-1,3,4-oxadiazin-2 -one. The amount of the foregoing blowing agents will vary depending on the agent and the desired foam density, and is readily determinable by one of ordinary skill in the art. In general, these blowing agents are used in an amount of about 0.1 to about 10 wt.% of the total composition.

In one embodiment the chemical blowing agent comprises a dihyrooxadiazinone. Dihydrooxadiazinones have been described in the following U.S. Pat. Nos.: 4,097,425, 4,097,671, 4,158,094, 4,160,088, and 4,163,037. Some exemplary dihydrooxadiazinones are, for example: 5,6-dimethyl-3,6-dihydro-1,3,4-oxadiazin-2-one, 5,6,6-trimethyl-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-ethyl-6-methoxy-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-phenyl-3,6-dihydro-1,3,4-oxidiazine-2-one, 5,6-diphenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-(p-bromophenyl)-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-phenyl-6-methyl-3,6-dihydro-1,3,4-oxadiazin-2-one, 5,6-bis(p-methoxylphenyl)-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-napthyl-3,6-dihydro-1,3,4-oxadiazin-2-one, 5-(o,o,p-tribromophenyl)-6-propyl-3,6-dihydro-1,3,4-oxadiazin-2-

one, 5-(p-hydroxyphenyl)-3,6-dihydro-1,3,4-oxadiazin-2-one, 5.phenyl-6,6-cyclopentylene-3,6-dihydro-1,3,4-oxadiazin-2-one and combinations of one or more of the foregoing.

In producing expandable composition, a variety of procedures may be used to combine the polymer blend or polymer and the chemical blowing agent. The polymer or blend of polymers may be contacted with the blowing agent while the blowing agent is in a molten state but below its decomposition temperature. For example the polymer or blend of polymers and chemical blowing agent may be combined and heated to a temperature such that the blowing agent is in a molten state and thus is incorporated into the resin or blend. Thereafter the treated resin or blend may be cooled and can be stored until such time as it is used.

Another method of combining the polymer or polymer blend and molten blowing agent is to preheat the polymer or polymer blend to a temperature below the decomposition temperature of the blowing agent and add the blowing agent in its molten form, blend, cool and thereafter the expandable composition is ready for use.

In the process of this invention, for example, a blowing agent is impregnated under pressure in the resulting thermoplastic resin beads in an aqueous suspension. A suspending agent is preferred to be added to the aqueous suspension in order to prevent bonding or coalescing of the thermoplastic resin beads during impregnation with the blowing agent. Examples suspending agents are organic compounds such as polyvinyl alcohol, polyacrylic acid salt, polyvinyl pyrrolidone, carboxymethyl cellulose, calcium stearate and ethylene-bis stearamide, and, sparingly, water-soluble fine powders of inorganic compounds such as calcium pyrophosphate, calcium phosphate, calcium carbonate, magnesium carbonate, magnesium phosphate, magnesium pyrophosphate and magnesium oxide. When an inorganic compound is used as the suspending agent in the process of this invention, it should be desirably used together with a surface active agent such as sodium dodecylbenzenesulfonate.

Easily volatilizable blowing agents are used in the process of this invention. Examples of blowing agents include aliphatic hydrocarbons such as propane, n-butane, i-butane,

n-pentane isopentane and n-hexane; cycloaliphatic hydrocarbons such as cyclopentane and cyclohexane; and halogenated hydrocarbons such as methyl chloride, ethyl chloride, dichlorodifluoromethane, chlorodifluoromethane and trichlorofluoromethane. These blowing agents are used in an amount of generally in the range of from 1 to 40, preferably up to 30 parts by weight based on 100 parts by weight of the thermoplastic interpolymer resin beads and blowing agent. A small amount for example, 1 to 5% by weight, of an organic solvent such as toluene or xylene, may be used together therewith.

The impregnation of the blowing agent is performed, for example, by suspending the polymerizable ingredients in water containing the suspending agent in an autoclave, heating the suspension, and introducing the blowing agent, e.g., under pressure, before or after the interpolymer beads are formed. This procedure affords expandable thermoplastic resin beads.

Various other modifications include spraying the polymer or polymer blend with a solution of the blowing agent and thereafter flashing off the solvent thus coating the blowing agent onto and within the polymer or polymer blend. Another alternative is to pass strands of resin through a solution of molten blowing agent and thereafter chopping the strands to produce a pelleted expandable composition. Alternatively one may optionally use the powder form of the blowing agent so long as it is substantially uniformly distributed throughout the resin.

For purposes of economics, it is sometimes advantageous to incorporate a chemical blowing agent into the polymer or polymer blend at relatively high concentrations to make a concentrate. Some chemical blowing agents, for example, 5-phenyl-3,6-dihydro-1,3,4-oxadiazin-2-one, act as plasticizers. Taking advantage of this property, the glass transition temperature of the polymer or polymer blend can be lowered to permit the polymer or polymer blend to be processed at low temperatures. Therefore concentrates containing from about 15-50% by weight of the blowing agent in the polymer or polymer blend can be made without decomposing the blowing agent. Such concentrates can be blended with the polymer or polymer blend by conventional techniques to yield a homogeneous expandable composition.

Thereafter, upon processing the expandable composition, an expanded composition is produced at temperatures suitable to decompose the blowing agent and yet at temperatures equal to or above the glass transition temperatures of the polymer or polymer blend.

As referred to above the expandable composition, in some embodiments, is stored and expanded at a later time. Alternatively the composition may be expanded when exiting the extruder. In either case the expanded composition may be expanded to a result in a desired shape. Alternatively, the expanded composition may be trimmed to form the desired shape. Two or more sections of expanded material may be adhered form a single piece, optionally through the use of an adhesive as taught, for example, in U.S. Patent No. 5,798,160. The expanded composition may also be laminated with a sheet or film to form a composite material.

In another embodiment of the present invention a porogen may be incorporated in the thermoplastic material such that when the porogen is burned out of the thermoplastic material there are generally spherically shaped voids left in the thermoplastic material have a mean size distribution of from between 1 and 150 nm or in another embodiment between about 1 and 50 nm. While not being bound by theory, it is thought that the following events occur during the processing of solutions containing a matrix precursor and a porogen. The solution of matrix precursor and porogen is applied to a substrate by a method such as spin coating. During this application some of the solvent evaporates leaving a more concentrated solution on the substrate. The coated substrate is then heated on a hot plate to remove most of the remaining solvent(s) leaving the porogen dispersed in the matrix precursor. During the solvent removal process and/or during subsequent thermal processing, the porogen phase separates from the matrix precursor. This phase separation may be driven by loss of solvent (concentration effect and/or change in solubility parameter of the solution), increases in molecular weight of the matrix precursor, assembly or aggregation of sufficient porogen mass in a specific location, or combinations thereof. With further heat treatments, the matrix becomes more fully cured. At an elevated temperature the porogen begins to decompose into fragments which can diffuse out of the coated film leaving behind a pore, thus forming a porous matrix. Porogens, methods of making

porogens and matrices formed using porogens are well known in the art and are described for example in U.S. Patents No.: 6,887,910; 6,653,358; and, 6,630,520, each of which is herein incorporated by reference in their entirety, as though set forth in full.

Representative examples of polymers, co-polymers and blends suitable for use in the annular articles of the present invention are listed below:

A. High Tg Polymer Blends of A Sulfone Based Polymer or Blend; a Silicone Co-polymer; and, a Resorcinol Derived Polyaryl Ester.

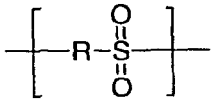
Disclosed herein are electrical connectors comprising a polymers blend, wherein some or all of one surface of the polymer blend is coated with a covering, wherein the covering material is of a different composition than the polymer blend, and, wherein the polymer blend comprises: a) a first resin selected from the group of polysulfones (PSu), poly(ether sulfone) (PES) poly(phenylene ether sulfone)s (PPSU) having a high glass transition temperature (Tg > 180 °C), b) a silicone copolymer, for instance silicone polyimide or silicone polycarbonate; and optionally, c) a resorcinol based polyarylate, wherein the blend has surprisingly low heat release values.

1. The Polysulfone, Polyether Sulfone And Polyphenylene Ether Sulfone Component Of The Blend

Polysulfones, poly(ether sulfone)s and poly(phenylene ether sulfone)s which are useful in the articles described herein are thermoplastic resins described, for example, in U.S. patents No.: 3,634,355, 4,008,203, 4,108,837 and 4,175,175.

Polysulfones, poly(ether sulfone)s and poly(phenylene ether sulfone)s are linear thermoplastic polymers that possess a number of attractive features such as high temperature resistance, good electrical properties, and good hydrolytic stability.

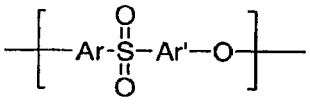
Polysulfones comprise repeating units having the structure of Formula I:



(I)

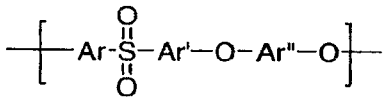
wherein R is an aromatic group comprising carbon-carbon single bonds, carbon-oxygen-carbon bonds or carbon-carbon and carbon-oxygen-carbon single bonds and the single bonds form a portion of the polymer backbone.

Poly(ether sulfone)s comprise repeating units having both an ether linkage and a sulfone linkage in the backbone of the polymer as shown in Formula II:



(II)

wherein Ar and Ar' are aromatic groups which may be the same or different. Ar and Ar' may be the same or different. When Ar and Ar' are both phenylene the polymer is known as poly(phenylene ether sulfone). When Ar and Ar' are both arylene the polymer is known as poly(arylene ether sulfone). The number of sulfone linkages and the number of ether linkages may be the same or different. An exemplary structure demonstrating when the number of sulfone linkages differ from the number of ether linkages is shown in Formula (III):



(III)

wherein Ar, Ar' and Ar" are aromatic groups which may be the same or different. Ar, Ar' and Ar" may be the same or different, for instance, Ar and Ar' may both be phenylene and Ar" may be a bis(1,4-phenylene)isopropyl group.

A variety of polysulfones and poly(ether sulfone)s are commercially available, including the polycondensation product of dihydroxy diphenyl sulfone with dichloro diphenyl sulfone, and the polycondensation product of bisphenol-A and or biphenol with dichloro diphenyl sulfone. Examples of commercially available resins include RADEL R, RADEL A, and UDEL, available from Solvay, Inc., and ULTRASON E, available from BASF Co.

Methods for the preparation of polysulfones and poly(ether sulfones) are widely known and several suitable processes have been well described in the art. Two

methods, the carbonate method and the alkali metal hydroxide method, are known to the skilled artisan. In the alkali metal hydroxide method, a double alkali metal salt of a dihydric phenol is contacted with a dihalobenzenoid compound in the presence of a dipolar, aprotic solvent under substantially anhydrous conditions. The carbonate method, in which a dihydric phenol and a dihalobenzenoid compound are heated, for example, with sodium carbonate or bicarbonate and a second alkali metal carbonate or bicarbonate is also disclosed in the art, for example in US Patents 4,176,222. Alternatively, the polysulfone and poly(ether sulfone) may be prepared by any of the variety of methods known in the art.

The molecular weight of the polysulfone or poly(ether sulfone), as indicated by reduced viscosity data in an appropriate solvent such as methylene chloride, chloroform, N-methylpyrrolidone, or the like, can be greater than or equal to about 0.3 dl/g, or, more specifically, greater than or equal to about 0.4 dl/g and, typically, will not exceed about 1.5 dl/g.

In some instances the polysulfone or poly(ether sulfone) weight average molecular weight can be about 10,000 to about 100,000 as determined by gel permeation chromatography using ASTM METHOD D5296. Polysulfones and poly(ether sulfone)s may have glass transition temperatures of about 180 °C to about 250 °C in some instances. When the polysulfones, poly(ethersulfone)s and poly(phenylene ether sulfone)s are blended with the resins described herein the polysulfone, poly(ether sulfone) and poly(phenylene ether) sulfone will have a glass transition temperature (Tg) greater than or equal to about 180 °C. Polysulfone resins are further described in ASTM method D6394 Standard Specification for Sulfone Plastics.

In some instances polysulfones, poly(ethersulfone)s and poly(phenylene ether sulfone)s and blends thereof, will have a hydrogen to carbon atom ratio (H/C) of less than or equal to about 0.85. Without being bound by theory polymers with higher carbon content relative to hydrogen content, that is a low ratio of hydrogen to carbon atoms, often show improved FR performance. These polymers have lower fuel value and may give off less energy when burned. They may also resist burning through a tendency to form an insulating char layer between the polymeric fuel and the source

of ignition. Independent of any specific mechanism or mode of action it has been observed that such polymers, with a low H/C ratio, have superior flame resistance. In some instances the H/C ratio can be less than or equal to 0.75 or less than 0.65. In other instances a H/C ratio of greater than or equal to about 0.4 is preferred in order to give polymeric structures with sufficient flexible linkages to achieve melt processability. The H/C ratio of a given polymer or copolymer can be determined from its chemical structure by a count of carbon and hydrogen atoms independent of any other atoms present in the chemical repeat unit.

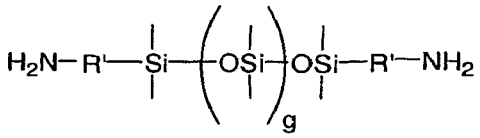
In the polymer blend the polysulfones, poly(ether sulfone)s and poly(phenylene ether sulfone)s and blends thereof may be present in amounts of about 1 to about 99 weight percent, based on the total weight of the polymer blend. Within this range, the amount of the polysulfones, poly(ether sulfone)s, and poly(phenylene ether sulfone)s and mixtures thereof may be greater than or equal to about 20 weight percent, more specifically greater than or equal to about 50 weight percent, and even more specifically greater than or equal to about 70 weight percent. The skilled artisan will appreciate that the polysulfones, poly(ether sulfones), and poly(phenylene ether sulfone)s and mixtures thereof may be present in a percentage by weight of the total polymer blend of any real number between about 1 and about 99 weight percent, and particularly from 1 to 70 weight percent.

2. The Silicone Component Of The Blend

The silicone copolymer comprises any siloxane copolymer effective to improve the heat release performance of the composition. In some instances siloxane copolymers of polyetherimides, polyetherimide sulfones, polysulfones, poly(phenylene ether sulfone)s, poly(ether sulfone)s or poly(phenylene ether)s maybe used. In some instances, siloxane polyetherimide copolymers, or siloxane polycarbonate copolymers may be effective in reducing heat release and improving flow rate performance. Mixtures of different types of siloxane copolymers are also contemplated. In one embodiment, the siloxane copolymer comprises about 5 to about 70 wt% and in other instances 20 to about 50 wt% siloxane content with respect to the total weight of the copolymer.

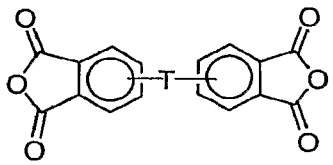
The block length of the siloxane segment of the copolymer may be of any effective length. In some examples, the block length may be about 2 to about 70 siloxane repeating units. In other instances the siloxane block length may be about 5 to about 50 repeating units. In many instances dimethyl siloxanes may be used.

Siloxane polyetherimide copolymers are a specific embodiment of the siloxane copolymer that may be used in the polymer blend. Examples of such siloxane polyetherimide copolymers are shown in US Patents No. 4,404,350, 4,808,686 and 4,690,997. In one instance the siloxane polyetherimide copolymer can be prepared in a manner similar to that used for polyetherimides, except that a portion, or all, of the organic diamine reactant is replaced by an amine-terminated organo siloxane, for example, of Formula IV wherein g is an integer having a value of 1 to about 50, or, more specifically, about 5 to about 30 and R' is an aryl, alkyl or aryl alky group having 2 to about 20 carbon atoms.



Formula IV

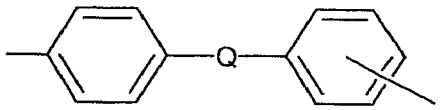
The siloxane polyetherimide copolymer can be prepared by any of the methods well known to those skilled in the art, including the reaction of an aromatic bis(ether anhydride) of the Formula V



(V)

wherein T is -O-, -S-, -SO_2- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions, and wherein Z includes, but is not limited to substituted or unsubstituted divalent organic radicals such as: (a) aromatic hydrocarbon radicals having about 6 to about 20 carbon atoms and halogenated derivatives thereof; (b) straight or branched chain

alkylene radicals having about 2 to about 20 carbon atoms; (c) cycloalkylene radicals having about 3 to about 20 carbon atoms, or (d) divalent radicals of the general Formula VI



(VI)

wherein Q includes but is not limited to a divalent group selected from the group consisting of -O-, -S-, -C(O)-, $-SO_2-$, -SO-, $-C_yH_{2y}-$ (y being an integer from 1 to 8), and fluorinated derivatives thereof, including perfluoroalkylene groups, with an organic diamine of the formula VII

$H_2N-R^1-NH_2$ (VII)

wherein group R^1 in formula VII includes, but is not limited to, substituted or unsubstituted divalent organic radicals such as: (a) aromatic hydrocarbon radicals having about 6 to about 24 carbon atoms and halogenated derivatives thereof; (b) straight or branched chain alkylene radicals having about 2 to about 20 carbon atoms; (c) cycloalkylene radicals having about 3 to about 20 carbon atoms, or (d) divalent radicals of the general formula VI.

Examples of specific aromatic bis anhydrides and organic diamines are disclosed, for example, in US Patents 3,972,902 and 4,455,410. Illustrative examples of aromatic bis anhydride of formula (XIV) include:

3,3-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride;

2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; and,

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride,

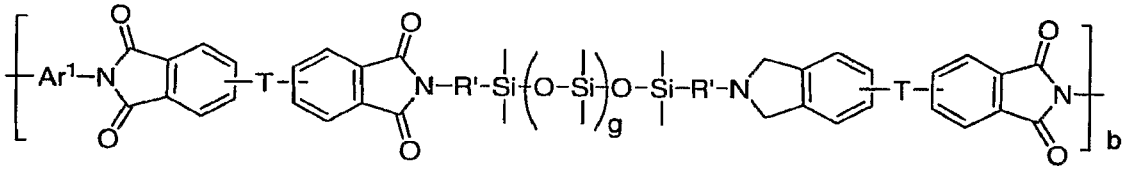
as well as mixtures thereof.

Examples of suitable diamines, in addition to the siloxane diamines described above, include ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylenetertramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2, 2-dimethylpropylenediamine, N-methyl-bis (3-aminopropyl) amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis(3-aminopropyl) sulfide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, m-xylylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl-4,6-diethyl-1,3-phenylene-diamine, benzidine, 3,3'-dimethylbenzidine, 3,3'–dimethoxybenzidine, 1,5-diaminonaphthalene, bis(4-aminophenyl) methane, bis(2-chloro-4-amino-3, 5-diethylphenyl) methane, bis(4-

aminophenyl) propane, 2,4-bis(amino-t-butyl) toluene, bis(p-amino-t-butylphenyl) ether, bis(p-methyl-o-aminophenyl) benzene, bis(p-methyl-o-aminopentyl) benzene, 1, 3-diamino-4-isopropylbenzene, bis(4-aminophenyl) sulfide, bis (4-aminophenyl) sulfone, bis(4-aminophenyl) ether and combinations comprising two or more of the foregoing. A specific example of a siloxane diamine is 1,3-bis(3-aminopropyl) tetramethyldisiloxane. In one embodiment the diamino compounds used in conjunction with the siloxane diamine are aromatic diamines, especially m- and p-phenylenediamine, sulfonyl dianiline and mixtures thereof.

Some siloxane polyetherimide copolymers may be formed by reaction of an organic diamine, or mixture of diamines, of formula VII and the amine-terminated organo siloxane of formula IV as mentioned above. The diamino components may be physically mixed prior to reaction with the bis-anhydride(s), thus forming a substantially random copolymer. Alternatively block or alternating copolymers may be formed by selective reaction of VII and IV with dianhydrides, for example those of formula V, to make polyimide blocks that are subsequently reacted together. In another instance the siloxane used to prepare the polyetherimde copolymer may have anhydride rather than amine functional end groups.

In one instance the siloxane polyetherimide copolymer can be of formula VIII wherein T, R' and g are described as above, b has a value of about 5 to about 100 and Ar^1 is an aryl or alkyl aryl group having 6 to about 36 carbons .



Formula VIII

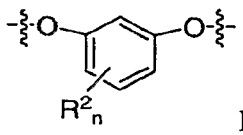
In some siloxane polyetherimide copolymers the diamine component of the siloxane polyetherimide copolymers may contain about 20 to 50 mole % of the amine-terminated organo siloxane of formula IV and about 50 to 80 mole % of the organic diamine of formula VII. In some siloxane copolymers, the siloxane component is

derived from about 25 to about 40 mole % of an amine or anhydride terminated organo siloxane.

The silicone copolymer component of the polymer blend may be present in an amount of about 0.1 to about 40 weight percent or alternatively from about 0.1 to about 20 weight percent with respect to the total weight of the polymer blend. Within this range, the silicone copolymer may also be present in an amount 0.1 to about 10%, further from 0.5 to about 5.0%.

3. The Resorcinol Based Polyarylate Component of the Blend

The resorcinol based polyarylate is a polymer comprising arylate polyester structural units that are the reaction product of a diphenol and an aromatic dicarboxylic acid. At least a portion of the arylate polyester structural units comprise a 1,3-dihydroxybenzene group, as illustrated in Formula I, commonly referred to throughout this specification as resorcinol or resorcinol group. Resorcinol or resorcinol group as used herein should be understood to include both unsubstituted 1,3-dihydroxybenzene and substituted 1,3-dihydroxybenzenes unless explicitly stated otherwise.



Formula IX

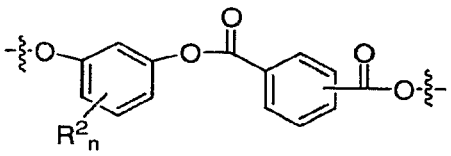
In Formula IX R^2 is independently at each occurrence a C_{1-12} alkyl, C_6-C_{24} aryl, C_7-C_{24} alkyl aryl, alkoxy or halogen, and n is 0-4.

In one embodiment, the resorcinol based polyarylate resin comprises greater than or equal to about 50 mole% of units derived from the reaction product of resorcinol with an aryl dicarboxylic acid or aryl dicarboxylic acid derivative suitable for the formation of aryl ester linkages, for example, carboxylic acid halides, carboxylic acid esters and carboxylic acid salts.

Suitable dicarboxylic acids include monocyclic and polycyclic aromatic dicarboxylic acids. Exemplary monocyclic dicarboxylic acids include isophthalic acid,

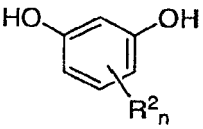
terephthalic acid, or mixtures of isophthalic and terephthalic acids. Polycyclic dicarboxylic acids include diphenyl dicarboxylic acid, diphenylether dicarboxylic acid, and naphthalenedicarboxylic acid, for example naphthalene-2,6-dicarboxylic acid.

Therefore, in one embodiment the polymer blend comprises a thermally stable polymers having resorcinol arylate polyester units as illustrated in Formula X wherein R^2 and n are as previously defined:



Formula X

Polymers comprising resorcinol arylate polyester units may be made by an interfacial polymerization method. To prepare polymers comprising resorcinol arylate polyester units substantially free of anhydride linkages a method can be employed wherein the first step combines a resorcinol group and a catalyst in a mixture of water and an organic solvent substantially immiscible with water. Suitable resorcinol compounds are of Formula XI:

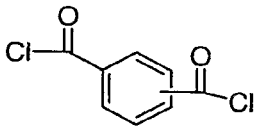


Formula XI

wherein R^2 is independently at each occurrence C_{1-12} alkyl, C_6-C_{24} aryl, C_7-C_{24} alkyl aryl, alkoxy or halogen, and n is 0-4. Alkyl groups, if present, are typically straight-chain, branched, or cyclic alkyl groups, and are most often located in the ortho position to both oxygen atoms although other ring locations are contemplated. Suitable C_{1-12} alkyl groups include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, butyl, iso-butyl, t-butyl, hexyl, cyclohexyl, nonyl, decyl, and aryl-substituted alkyl, including benzyl. In a particular embodiment an alkyl group is methyl. Suitable halogen groups are bromo, chloro, and fluoro. The value for n in various embodiments may be 0 to 3, in some embodiments 0 to 2, and in still other embodiments 0 to1. In one embodiment the resorcinol group is 2-methylresorcinol. In

another embodiment the resorcinol group is an unsubstituted resorcinol group in which n is zero. The method further comprises combining one catalyst with the reaction mixture. Said catalyst may be present in various embodiments at a total level of 0.01 to 10 mole %, and in some embodiments at a total level of 0.2 to 6 mole % based on total molar amount of acid chloride groups. Suitable catalysts comprise tertiary amines, quaternary ammonium salts, quaternary phosphonium salts, hexaalkylguanidinium salts, and mixtures thereof.

Suitable dicarboxylic acid dihalides may comprise aromatic dicarboxylic acid dichlorides derived from monocyclic moieties, illustrative examples of which include isophthaloyl dichloride, terephthaloyl dichloride, or mixtures of isophthaloyl and terephthaloyl dichlorides. Suitable dicarboxylic acid dihalides may also comprise aromatic dicarboxylic acid dichlorides derived from polycyclic moieties, illustrative examples of which include diphenyl dicarboxylic acid dichloride, diphenylether dicarboxylic acid dichloride, and naphthalenedicarboxylic acid dichloride, especially naphthalene-2,6-dicarboxylic acid dichloride; or from mixtures of monocyclic and polycyclic aromatic dicarboxylic acid dichlorides. In one embodiment the dicarboxylic acid dichloride comprises mixtures of isophthaloyl and/or terephthaloyl dichlorides as typically illustrated in Formula XII.



Formula XII

Either or both of isophthaloyl and terephthaloyl dichlorides may be present. In some embodiments the dicarboxylic acid dichlorides comprise mixtures of isophthaloyl and terephthaloyl dichloride in a molar ratio of isophthaloyl to terephthaloyl of about 0.25-4.0:1; in other embodiments the molar ratio is about 0.4-2.5:1; and in still other embodiments the molar ratio is about 0.67-1.5:1.

Dicarboxylic acid halides provide only one method of preparing the polymers mentioned herein. Other routes to make the resorcinol arylate linkages are also contemplated using, for example, the dicarboxylic acid, a dicarboxylic acid ester, especially an activated ester, or dicarboxylate salts or partial salts.

A one chain-stopper (also referred to sometimes hereinafter as capping agent) may also be used. A purpose of adding a chain-stopper is to limit the molecular weight of polymer comprising resorcinol arylate polyester chain members, thus providing polymer with controlled molecular weight and favorable processability. Typically, a chain-stopper is added when the resorcinol arylate-containing polymer is not required to have reactive end-groups for further application. In the absence of chain-stopper resorcinol arylate-containing polymer may be either used in solution or recovered from solution for subsequent use such as in copolymer formation which may require the presence of reactive end-groups, typically hydroxy, on the resorcinol-arylate polyester segments. A chain-stopper may be a mono-phenolic compound, a mono-carboxylic acid chloride, a mono-chloroformates or a combination of two or more of the foregoing. Typically, the chain-stopper may be present in quantities of 0.05 to 10 mole %, based on resorcinol in the case of mono-phenolic compounds and based on acid dichlorides in the case mono-carboxylic acid chlorides and/or mono-chloroformates.

Suitable mono-phenolic compounds include monocyclic phenols, such as phenol, C_1-C_{22} alkyl-substituted phenols, p-cumyl-phenol, p-tertiary-butyl phenol, hydroxy diphenyl; monoethers of diphenols, such as p-methoxyphenol. Alkyl-substituted phenols include those with branched chain alkyl substituents having 8 to 9 carbon atoms as described in U.S. Patent 4,334,053. In some embodiments mono-phenolic chain-stoppers are phenol, p-cumylphenol, and resorcinol monobenzoate.

Suitable mono-carboxylic acid chlorides include monocyclic, mono-carboxylic acid chlorides, such as benzoyl chloride, C_1-C_{22} alkyl-substituted benzoyl chloride, toluoyl chloride, halogen-substituted benzoyl chloride, bromobenzoyl chloride, cinnamoyl chloride, 4-nadimidobenzoyl chloride, and mixtures thereof; polycyclic, mono-carboxylic acid chlorides, such as trimellitic anhydride chloride, and naphthoyl chloride; and mixtures of monocyclic and polycyclic mono-carboxylic acid chlorides. The chlorides of aliphatic monocarboxylic acids with up to 22 carbon atoms are also suitable. Functionalized chlorides of aliphatic monocarboxylic acids, such as acryloyl chloride and methacryoyl chloride, are also suitable. Suitable mono-chloroformates include monocyclic, mono-chloroformates, such as phenyl chloroformate, alkyl-

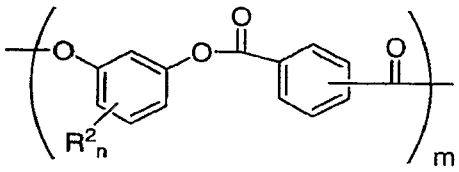
substituted phenyl chloroformate, p-cumyl phenyl chloroformate, toluene chloroformate, and mixtures thereof.

A chain-stopper can be combined together with the resorcinol, can be contained in the solution of dicarboxylic acid dichlorides, or can be added to the reaction mixture after production of a precondensate. If mono-carboxylic acid chlorides and/or mono-chloroformates are used as chain-stoppers, they are often introduced together with dicarboxylic acid dichlorides. These chain-stoppers can also be added to the reaction mixture at a moment when the chlorides of dicarboxylic acid have already reacted substantially or to completion. If phenolic compounds are used as chain-stoppers, they can be added in one embodiment to the reaction mixture during the reaction, or, in, another embodiment, before the beginning of the reaction between resorcinol and acid dichloride. When hydroxy-terminated resorcinol arylate-containing precondensate or oligomers are prepared, then chain-stopper may be absent or only present in small amounts to aid control of oligomer molecular weight.

In another embodiment a branching agent such as a trifunctional or higher functional carboxylic acid chloride and/or trifunctional or higher functional phenol may be included. Such branching agents, if included, can typically be used in quantities of 0.005 to 1 mole %, based on dicarboxylic acid dichlorides or resorcinol used, respectively. Suitable branching agents include, for example, trifunctional or higher carboxylic acid chlorides, such as trimesic acid tri acid chloride, 3,3´,4,4´-benzophenone tetracarboxylic acid tetrachloride, 1,4,5,8-naphthalene tetracarboxylic acid tetrachloride or pyromellitic acid tetrachloride, and trifunctional or higher phenols, such as 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-2-heptene, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenyl methane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenylisopropyl)-phenol, tetra-(4-hydroxyphenyl)-methane, 2,6-bis-(2-hydroxy-5-methylbenzyl)-4-methyl phenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, tetra-(4-[4-hydroxyphenylisopropyl]-phenoxy)-methane, 1,4-bis-[(4,4-dihydroxytriphenyl)methyl]-benzene. Phenolic branching agents may be introduced

first with the resorcinol moieties while acid chloride branching agents may be introduced together with acid dichlorides.

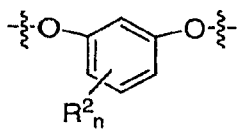
In one of its embodiments articles of manufacture comprise thermally stable resorcinol arylate polyesters made by the described method and substantially free of anhydride linkages linking at least two mers of the polyester chain. In a particular embodiment said polyesters comprise dicarboxylic acid residues derived from a mixture of iso- and terephthalic acids as illustrated in Formula XIII:



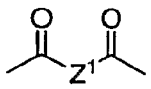
Formula XIII

wherein R^2 is independently at each occurrence a C_{1-12} alkyl, C_6-C_{24} aryl, alkyl aryl, alkoxy or halogen, n is 0-4, and m is greater than or equal to about 5. In various embodiments n is zero and m is about 10 to about 300. The molar ratio of isophthalate to terephthalate is in one embodiment about 0.25-4.0:1, in another embodiment about 0.4-2.5:1, and in still another embodiment about 0.67-1.5:1. Substantially free of anhydride linkages means that said polyesters show decrease in molecular weight in one embodiment of less than 30% and in another embodiment of less than 10% upon heating said polymer at a temperature of about 280-290°C for five minutes.

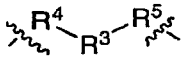
Also included are articles comprising a resorcinol arylate copolyesters containing soft-block segments as disclosed in commonly owned U.S. Patent No. 5,916,997. The term soft-block as used herein, indicates that some segments of the polymers are made from non-aromatic monomer units. Such non-aromatic monomer units are generally aliphatic and are known to impart flexibility to the soft-block-containing polymers. The copolymers include those comprising structural units of Formulas IX, XIV, and XV:



Formula IX



Formula XIV



Formula XV

wherein R^2 and n are as previously defined, Z^1 is a divalent aromatic radical, R^3 is a C_{3-20} straight chain alkylene, C_{3-10} branched alkylene, or C_{4-10} cyclo- or bicycloalkylene group, and R^4 and R^5 each independently represent

 or $-CH_2-O-$,

wherein Formula XV contributes about 1 to about 45 mole percent to the ester linkages of the polyester. Additional embodiments provide a composition wherein Formula XV contributes in various embodiments about 5 to about 40 mole percent to the ester linkages of the polyester, and in other embodiments about 5 to about 20 mole percent to the ester linkages of the polyester. Another embodiment provides a composition wherein R^3 represents in one embodiment C_{3-14} straight chain alkylene, or C_{5-6} cycloalkylene, and in another embodiment R^3 represents C_{3-10} straight-chain alkylene or C_6-cycloalkylene. Formula XIV represents an aromatic dicarboxylic acid residue. The divalent aromatic radical Z^1 in Formula XIV may be derived in various embodiments from a suitable dicarboxylic acid residues as defined hereinabove, and in some embodiments comprises 1,3-phenylene, 1,4-phenylene, or 2,6-naphthylene or a combination of two or more of the foregoing. In various embodiments Z^1 comprises

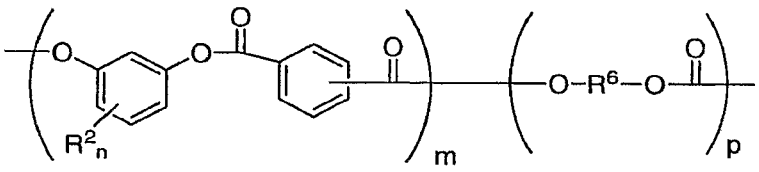
greater than or equal to about 40 mole percent 1,3-phenylene. In various embodiments of copolyesters containing soft-block chain members n in Formula IX is zero.

In another of its embodiments the resorcinol based polyarylate can be a block copolyestercarbonate comprising resorcinol arylate-containing block segments in combination with organic carbonate block segments. The segments comprising resorcinol arylate chain members in such copolymers are substantially free of anhydride linkages. Substantially free of anhydride linkages means that the copolyestercarbonates show decrease in molecular weight in one embodiment of less than 10% and in another embodiment of less than 5% upon heating said copolyestercarbonate at a temperature of about 280-290°C for five minutes.

The carbonate block segments contain carbonate linkages derived from reaction of a bisphenol and a carbonate forming species, such as phosgene, making a polyester carbonate copolymer. For example, the resorcinol polyarylate carbonate copolymers can comprise the reaction products of iso- and terephthalic acid, resorcinol and bisphenol A and phosgene. The resorcinol polyester carbonate copolymer can be made in such a way that the number of bisphenol dicarboxylic ester linkages is minimized, for example by pre-reacting the resorcinol with the dicarboxylic acid to form an aryl polyester block and then reacting a said block with the bisphenol and carbonate to form the polycarbonate part of the copolymer.

For best effect, resorcinol ester content (REC) in the resorcinol polyester carbonate should be greater than or equal to about 50 mole % of the polymer linkages being derived from resorcinol. In some instances REC of greater than or equal to about 75 mole%, or even as high as about 90 or 100 mole% resorcinol derived linkages may be desired depending on the application.

The block copolyestercarbonates include those comprising alternating arylate and organic carbonate blocks, typically as illustrated in Formula XVI, wherein R^2 and n are as previously defined, and R^6 is a divalent organic radical:



Formula XVI

The arylate blocks have a degree of polymerization (DP), represented by m, that is in one embodiment greater than or equal to about 4, in another embodiment greater than or equal to about 10, in another embodiment greater than or equal to about 20 and in still another embodiment about 30 to about 150. The DP of the organic carbonate blocks, represented by p, is in one embodiment greater than or equal to about 2, in another embodiment about 10 to about 20 and in still another embodiment about 2 to about 200. The distribution of the blocks may be such as to provide a copolymer having any desired weight proportion of arylate blocks in relation to carbonate blocks. In general, the content of arylate blocks is in one embodiment about 10 to about 95% by weight and in another embodiment about 50 to about 95% by weight with respect to the total weight of the polymer.

Although a mixture of iso- and terephthalate is illustrated in Formula XVI, the dicarboxylic acid residues in the arylate blocks may be derived from any suitable dicarboxylic acid residue, as defined hereinabove, or mixture of suitable dicarboxylic acid residues, including those derived from aliphatic diacid dichlorides (so-called "soft-block" segments). In various embodiments n is zero and the arylate blocks comprise dicarboxylic acid residues derived from a mixture of iso- and terephthalic acid residues, wherein the molar ratio of isophthalate to terephthalate is in one embodiment about 0.25 to 4.0:1, in another embodiment about 0.4 to2.5:1, and in still another embodiment about 0.67 to1.5:1.

In the organic carbonate blocks, each R^6 is independently at each occurrence a divalent organic radical. In various embodiments said radical comprises a dihydroxy-substituted aromatic hydrocarbon, and greater than or equal to about 60 percent of the total number of R^6 groups in the polymer are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Suitable R^6 radicals

include m-phenylene, p-phenylene, 4,4'-biphenylene, 4,4'-bi(3,5-dimethyl)-phenylene, 2,2-bis(4-phenylene)propane, 6,6'-(3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indan]) and similar radicals such as those which correspond to the dihydroxy-substituted aromatic hydrocarbons disclosed by name or formula (generic or specific) in U.S. Patent 4,217,438.

In some embodiments each R^6 is an aromatic organic radical and in other embodiments a radical of Formula XVII:

$$——A^1—Y—A^2——$$

Formula XVII

wherein each A^1 and A^2 is a monocyclic divalent aryl radical and Y is a bridging radical in which one or two carbon atoms separate A^1 and A^2. The free valence bonds in Formula XVII are usually in the meta or para positions of A^1 and A^2 in relation to Y. Compounds in which R^6 has Formula XVII are bisphenols, and for the sake of brevity the term "bisphenol" is sometimes used herein to designate the dihydroxy-substituted aromatic hydrocarbons. It should be understood, however, that non-bisphenol compounds of this type may also be employed as appropriate.

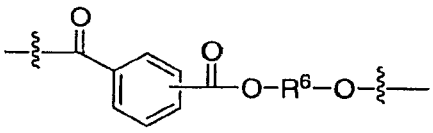
In Formula XVII, A^1 and A^2 typically represent unsubstituted phenylene or substituted derivatives thereof, illustrative substituents (one or more) being alkyl, alkenyl, and halogen (particularly bromine). In one embodiment unsubstituted phenylene radicals are preferred. Both A^1 and A^2 are often p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

The bridging radical, Y, is one in which one or two atoms, separate A^1 from A^2. In a particular embodiment one atom separates A^1 from A^2. Illustrative radicals of this type are -O-, -S-, -SO- or -SO_2-, methylene, cyclohexyl methylene, 2-[2.2.1]-bicycloheptyl methylene, ethylene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene, and like radicals.

In some embodiments gem-alkylene (commonly known as "alkylidene") radicals are preferred. Also included, however, are unsaturated radicals. In some embodiments the bisphenol is 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A or BPA), in which Y is isopropylidene and A^1 and A^2 are each p-phenylene. Depending upon the molar excess of resorcinol present in the reaction mixture, R^6 in the carbonate blocks may at least partially comprise resorcinol group. In other words, in some embodiments carbonate blocks of Formula X may comprise a resorcinol group in combination with at least one other dihydroxy-substituted aromatic hydrocarbon.

Diblock, triblock, and multiblock copolyestercarbonates are included. The chemical linkages between blocks comprising resorcinol arylate chain members and blocks comprising organic carbonate chain members may comprise at least one of

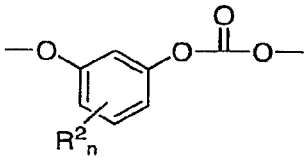
(a) an ester linkage between a suitable dicarboxylic acid residue of an arylate group and an —O—R^6—O— group of an organic carbonate group, for example as typically illustrated in Formula XVIII, wherein R^6 is as previously defined :



Formula XVIII

and

(b) a carbonate linkage between a diphenol residue of a resorcinol arylate group and a —(C=O)—O— group of an organic carbonate group as shown in Formula XIX, wherein R^2 and n are as previously defined :



Formula XIX

In one embodiment the copolyestercarbonate is substantially comprised of a diblock copolymer with a carbonate linkage between resorcinol arylate block and an organic carbonate block. In another embodiment the copolyestercarbonate is substantially comprised of a triblock carbonate-ester-carbonate copolymer with carbonate linkages between the resorcinol arylate block and organic carbonate end-blocks.

Copolyestercarbonates with a carbonate linkage between a thermally stable resorcinol arylate block and an organic carbonate block are typically prepared from resorcinol arylate-containing oligomers and containing in one embodiment at least one and in another embodiment at least two hydroxy-terminal sites. Said oligomers typically have weight average molecular weight in one embodiment of about 10,000 to about 40,000, and in another embodiment of about 15,000 to about 30,000. Thermally stable copolyestercarbonates may be prepared by reacting said resorcinol arylate-containing oligomers with phosgene, a chain-stopper, and a dihydroxy-substituted aromatic hydrocarbon in the presence of a catalyst such as a tertiary amine.

In one instance articles can comprise a blend of a resin selected from the group consisting of: polysulfones, poly(ethersulfone)s and poly(phenylene ether sulfone)s, and mixtures thereof; a silicone copolymer and a resorcinol based polyarylate wherein greater than or equal to 50 mole % of the aryl polyester linkages are aryl ester linkages derived from resorcinol.

The amount of resorcinol based polyarylate used in the polymer blends used to make articles can vary widely depending on the end use of the article. For example, when the article will be used in an end use where heat release or increase time to peak heat release are important, the amount of resorcinol ester containing polymer can be maximized to lower the heat release and lengthen the time period to peak heat release. In some instances resorcinol based polyarylate can be about 1 to about 50 weight percent of the polymer blend. Some compositions of note will have about 10 to about 50 weight percent resorcinol based polyarylate with respect to the total weight of the polymer blend.

In another embodiment, an article comprising a polymer blend of;

a) about 1 to about 99% by weight of a polysulfones, poly(ether sulfone)s and poly(phenylene ether sulfone)s or mixtures thereof;

b) about 0.1 to about 30% by weight of silicone copolymer;

c) about 99 to about 1% by weight of a resorcinol based polyarylate containing greater than or equal to about 50 mole% resorcinol derived linkages;

d) 0 to about 20% by weight of a metal oxide,

is contemplated wherein weight percent is with respect to the total weight of the polymer blend.

In other aspect an article comprising a polymer blend of

about 50 to about 99% by weight of a polysulfone, poly(ether sulfone), poly(phenylene ether sulfone)s or mixture thereof;

about 0.1 to about 10% by weight of a silicone copolymer;

about 1 to about 50% by weight of a resorcinol based polyarylate resin containing greater than or equal to about 50 mole% resorcinol derived linkages;

0 to about 20% by weight of a metal oxide; and

0 to about 2% by weight of a phosphorus containing stabilizer, is contemplated.

B. High Tg Blends of: a PEI, PI, PEIS, and Mixtures Thereof; a Silicone Copolymer; and, a Resorcinol Based Aryl Polyester Resin.

Combinations of silicone copolymers, for instance silicone polyetherimide copolymers or silicone polycarbonate copolymers, with high glass transition temperature (Tg) polyimide (PI), polyetherimide (PEI) or polyetherimide sulfone (PEIS) resins, and resorcinol based polyarylate have surprisingly low heat release values and improved solvent resistance.

The resorcinol derived aryl polyesters can also be a copolymer containing non-resorcinol based linkages, for instance a resorcinol – bisphenol-A copolyester carbonate. For best effect, resorcinol ester content (REC) should be greater than about 50 mole % of the polymer linkages being derived from resorcinol. Higher REC may be preferred. In some instances REC of greater than 75 mole %, or even as high as 90 or 100 mole% resorcinol derived linkages may be desired.

The amount of resorcinol ester containing polymer used in the flame retardant blend can vary widely using any effective amount to reduce heat release, increase time to peak heat release or to improve solvent resistance. In some instances resorcinol ester containing polymer can be about 1 wt% to about 80 wt% of the polymer blend. Some compositions of note will have 10-50% resorcinol based polyester. In other instances blends of polyetherimide or polyetherimide sulfone with high REC copolymers will have a single glass transition temperature (Tg) of about 150 to about 210 °C.

The resorcinol based polyarylate resin should contain greater than or equal to about 50 mole% of units derived from the reaction product of resorcinol, or functionalized resorcinol, with an aryl dicarboxylic acid or dicarboxylic acid derivatives suitable for the formation of aryl ester linkages, for example, carboxylic acid halides, carboxylic acid esters and carboxylic acid salts.

The resorcinol based polyarylates which can be used according to the present invention are further detailed herein for other polymer blends.

Copolyestercarbonates with at least one carbonate linkage between a thermally stable resorcinol arylate block and an organic carbonate block are typically prepared from resorcinol arylate-containing oligomers prepared by various embodiments of the invention and containing in one embodiment at least one and in another embodiment at least two hydroxy-terminal sites. Said oligomers typically have weight average molecular weight in one embodiment of about 10,000 to about 40,000, and in another embodiment of about 15,000 to about 30,000. Thermally stable copolyestercarbonates may be prepared by reacting said resorcinol arylate-containing oligomers with

phosgene, at least one chain-stopper, and at least one dihydroxy-substituted aromatic hydrocarbon in the presence of a catalyst such as a tertiary amine.

In one instance a polymer blend with improved flame retardance comprises a resin selected from the group consisting of polyimides, polyetherimides, polyetherimide sulfones, and mixtures thereof; a silicone copolymer and a resorcinol based aryl polyester resin wherein greater than or equal to 50 mole % of the aryl polyester linkages are aryl ester linkages derived from resorcinol. The term "polymer linkage" or "a polymer linkage" is defined as the reaction product of at least two monomers that form the polymer.

In some instances polyimides, polyetherimides, polyetherimide sulfones and mixtures thereof, will have a hydrogen atom to carbon atom ratio (H/C) of less than or equal to about 0.85 are of note. Polymers with higher carbon content relative to hydrogen content, that is a low ratio of hydrogen to carbon atoms, often show improved FR performance. These polymers have lower fuel value and may give off less energy when burned. They may also resist burning through a tendency to form an insulating char layer between the polymeric fuel and the source of ignition. Independent of any specific mechanism or mode of action it has been observed that such polymers, with a low H/C ratio, have superior flame resistance. In some instances the H/C ratio can be less than 0.85. In other instances a H/C ratio of greater than about 0.4 is preferred in order to give polymeric structures with sufficient flexible linkages to achieve melt processability. The H/C ratio of a given polymer or copolymer can be determined from its chemical structure by a count of carbon and hydrogen atoms independent of any other atoms present in the chemical repeat unit.

In some cases the flame retardant polymer blends, and articles made from them, will have 2 minute heat release of less than about 65 kW-min/m^2. In other instances the peak heat release will be less than about 65kW/m^2. A time to peak heat release of more than about 2 minute is also a beneficial aspect of certain compositions and articles made from them. In other instances a time to peak heat release time of greater than about 4 minutes may be achieved.

In some compositions the blend of polyimides, polyetherimides, polyetherimide sulfones or mixtures thereof with silicone copolymer and aryl polyester resin containing greater than or equal to about 50 mole% resorcinol derived linkages will be transparent. In one embodiment, the blend has a percent transmittance greater than about 50% as measured by ASTM method D1003 at a thickness of 2 millimeters. In other instances the percent haze of these transparent compositions, as measured by ASTM method D1003, will be less than about 25%. In other embodiments the percent transmittance will be greater than about 60% and the percent haze less than about 20%. In still other instances the composition and article made from it will have a transmittance of greater than about 50% and a haze value below about 25% with a peak heat release of less than or equal to 50 kW/m^2.

In the flame retardant blends the polyimides, polyetherimides, polyetherimide sulfones or mixtures thereof may be present in amounts of about 1 to about 99 weight percent, based on the total weight of the composition. Within this range, the amount of the polyimides, polyetherimides, polyetherimide sulfones or mixtures thereof may be greater than or equal to about 20, more specifically greater than or equal to about 50, or, even more specifically, greater than or equal to about 70 weight percent.

In another embodiment a composition comprises a flame retardant polymer blend of:

a) about 1 to about 99% by weight of a polyetherimide, polyetherimide sulfone and mixtures thereof,

b) about 99 to about 1% by weight of an aryl polyester resin containing greater than or equal to about 50 mole% resorcinol derived linkages,

c) about 0.1 to about 30% by weight of silicone copolymer

d) about 0 to about 20% by weight of a metal oxide,

wherein the weight percents are with respect to the total weight of the composition.

In other aspect a composition comprises a flame retardant polymer blend of;

about 50 to about 99% by weight of a polyetherimide or polyetherimide sulfone resin,

about 1 to about 50% by weight of a resorcinol based polyarylate containing greater than or equal to about 50 mole% resorcinol derived linkages,

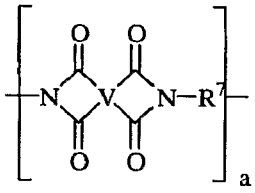
about 0.1 to about 10% by weight of silicone copolymer

about 0 to about 20% by weight of a metal oxide, and

0 to about 2% by weight of a phosphorus containing stabilizer,

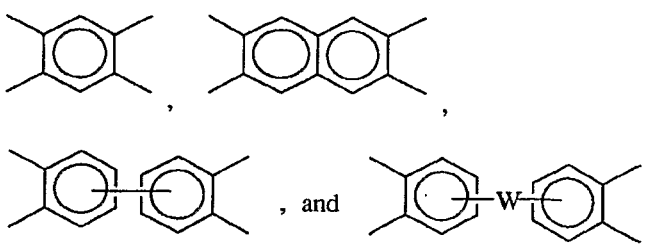
is contemplated.

Polyimides have the general formula (XX)



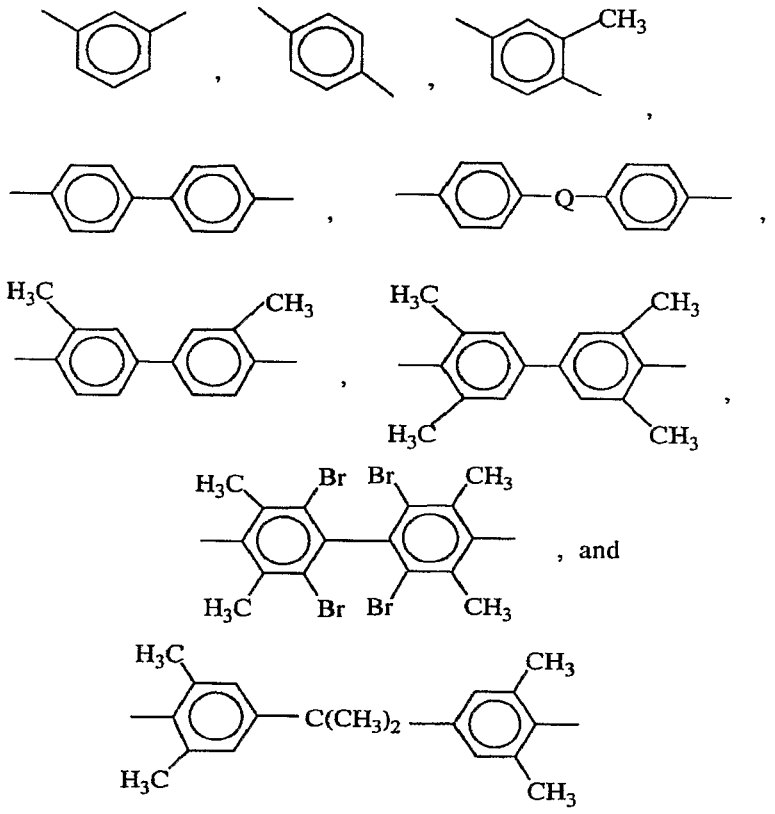
(Formula XX)

wherein a is more than 1, typically about 10 to about 1000 or more, or, more specifically about 10 to about 500; and wherein V is a tetravalent linker without limitation, as long as the linker does not impede synthesis or use of the polyimide. Suitable linkers include but are not limited to: (a) substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic and polycyclic groups having about 5 to about 50 carbon atoms, (b) substituted or unsubstituted, linear or branched, saturated or unsaturated alkyl groups having 1 to about 30 carbon atoms; or combinations thereof. Preferred linkers include but are not limited to tetravalent aromatic radicals of formula (XXI), such as



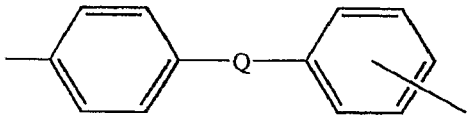
(Formula XXI)

wherein W is a divalent group selected from the group consisting of -O-, -S-, -C(O)-, SO_2-, -SO-, $-C_yH_{2y}-$ (y being an integer having a value of 1 to about 8), and fluoronated derivatives thereof, including perfluoroalkylene groups, or a group of the formula -O-Z-O- wherein the divalent bonds of the -W- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions, and wherein Z is defined as above. Z may comprise exemplary divalent radicals of formula (XXII).



(Formula XXII)

R^7 in formula (XX) includes but is not limited to substituted or unsubstituted divalent organic radicals such as: (a) aromatic hydrocarbon radicals having about 6 to about 24 carbon atoms and halogenated derivatives thereof; (b) straight or branched chain alkylene radicals having about 2 to about 20 carbon atoms; (c) cycloalkylene radicals having about 3 to about 24 carbon atoms, or (d) divalent radicals of the general formula (VI)

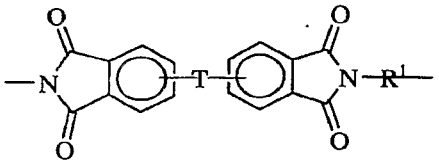


(Formula VI)

wherein Q is defined as above.

Some classes of polyimides include polyamidimides, polyetherimide sulfones and polyetherimides, particularly those polyetherimides known in the art which are melt processable, such as those whose preparation and properties are described in U.S. Patents 3,803,085 and 3,905,942.

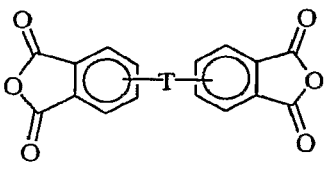
Polyetherimide resins may comprise more than 1, typically about 10 to about 1000 or more, or, more specifically, about 10 to about 500 structural units, of the formula (XXIII)



(Formula XXIII)

wherein T is -O- or a group of the formula -O-Z-O- wherein the divalent bonds of the -O- or the -O-Z-O- group are in the 3,3', 3,4', 4,3', or the 4,4' positions, and wherein Z is defined above. In one embodiment, the polyimide, polyetherimide or polyetherimide sulfone may be a copolymer. Mixtures of the polyimide, polyetherimide or polyetherimide sulfone may also be employed.

The polyetherimide can be prepared by any of the methods well known to those skilled in the art, including the reaction of an aromatic bis(ether anhydride) of the formula (XVIII)



(Formula V)

with an organic diamine of the formula (VII)

$H_2N\text{-}R^1\text{-}NH_2$ (Formula VII)

wherein T and R^1 are defined as described above.

Examples of specific aromatic bis anhydrides and organic diamines are disclosed, for example, in US Patents 3,972,902 and 4,455,410. Illustrative examples of aromatic bis anhydrides include:

3,3-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride;

2,2-bis[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride;

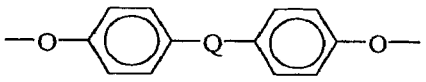
4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride; and, 4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride, as well as various mixtures thereof.

Another class of aromatic bis(ether anhydride)s included by formula (XVIII) above includes, but is not limited to, compounds wherein T is of the formula (XXIV)

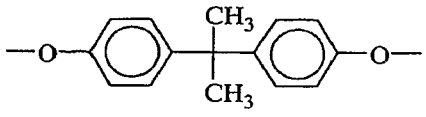


(Formula XXIV)

and the ether linkages, for example, are preferably in the 3,3', 3,4', 4,3', or 4,4' positions, and mixtures thereof, and where Q is as defined above.

Any diamino compound may be employed. Examples of suitable compounds are ethylenediamine, propylenediamine, trimethylenediamine, diethylenetriamine, triethylenetertramine, hexamethylenediamine, heptamethylenediamine, octamethylenediamine, nonamethylenediamine, decamethylenediamine, 1,12-dodecanediamine, 1,18-octadecanediamine, 3-methylheptamethylenediamine, 4,4-dimethylheptamethylenediamine, 4-methylnonamethylenediamine, 5-methylnonamethylenediamine, 2,5-dimethylhexamethylenediamine, 2,5-dimethylheptamethylenediamine, 2, 2-dimethylpropylenediamine, N-methyl-bis (3-aminopropyl) amine, 3-methoxyhexamethylenediamine, 1,2-bis(3-aminopropoxy) ethane, bis(3-aminopropyl) sulfide, 1,4-cyclohexanediamine, bis-(4-aminocyclohexyl) methane, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 2,6-diaminotoluene, m-xylylenediamine, p-xylylenediamine, 2-methyl-4,6-diethyl-1,3-phenylene-diamine, 5-methyl-4,6-diethyl-1,3-phenylene-diamine, benzidine, 3,3'-dimethylbenzidine, 3,3'–dimethoxybenzidine, 1,5-diaminonaphthalene, bis(4-aminophenyl) methane, bis(2-chloro-4-amino-3, 5-diethylphenyl) methane, bis(4-aminophenyl) propane, 2,4-bis(p-amino-t-butyl) toluene, bis(p-amino-t-butylphenyl) ether, bis(p-methyl-o-aminophenyl) benzene, bis(p-methyl-o-aminopentyl) benzene, 1, 3-diamino-4-isopropylbenzene, bis(4-aminophenyl) sulfide, bis (4-aminophenyl) sulfone, and bis(4-aminophenyl) ether. Mixtures of these compounds may also be used. The preferred diamino compounds are aromatic diamines, especially m- and p-phenylenediamine, sulfonyl dianiline and mixtures thereof.

In one embodiment, the polyetherimide resin comprises structural units according to formula (XVII) wherein each R is independently p-phenylene or m-phenylene or a mixture thereof and T is a divalent radical of the formula (XXV)



(Formula XXV)

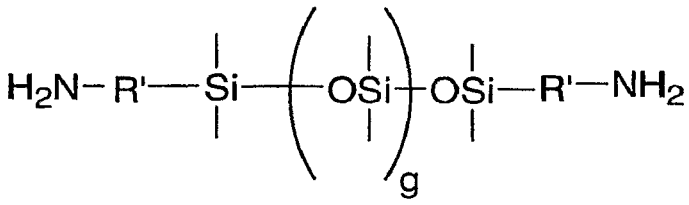
Included among the many methods of making the polyimides, particularly polyetherimides, are those disclosed in US Patents 3,847,867, 3,852,242, 3,803,085, 3905,942, 3,983,093, and 4,443,591. These patents mentioned for the purpose of teaching, by way of illustration, general and specific methods for preparing polyimides.

Polyimides, polyetherimides and polyetherimide sulfones may have a melt index of about 0.1 to about 10 grams per minute (g/min), as measured by American Society for Testing Materials (ASTM) D1238 at 340 to about 370°C, using a 6.6 kilogram (kg) weight. In a one embodiment, the polyetherimide resin has a weight average molecular weight (Mw) of about 10,000 to about 150,000 grams per mole (g/mole), as measured by gel permeation chromatography, using a polystyrene standard. In another embodiment the polyetherimide has Mw of 20,000 to 60,000. Such polyetherimide resins typically have an intrinsic viscosity greater than about 0.2 deciliters per gram (dl/g), or, more specifically, about 0.35 to about 0.7 dl/g as measured in m-cresol at 25°C. Examples of some polyetherimides useful in blends described herein are listed in ASTM D5205 "Standard Classification System for Polyetherimide (PEI) Materials".

The block length of the siloxane segment of the copolymer may be of any effective length. In some examples it may be of 2 to-70 siloxane repeating units. In other instances the siloxane block length may be about 5 to about 30 repeat units. In many instances dimethyl siloxanes may be used.

Siloxane polyetherimide copolymers are a specific embodiment of the siloxane copolymer that may be used. Examples of such siloxane polyetherimides are shown in US Patents 4,404,350, 4,808,686 and 4,690,997. In one instance polyetherimide siloxanes can be prepared in a manner similar to that used for polyetherimides, except that a portion, or all, of the organic diamine reactant is replaced by an amine-terminated organo siloxane, for example of the formula XXII wherein g is an integer

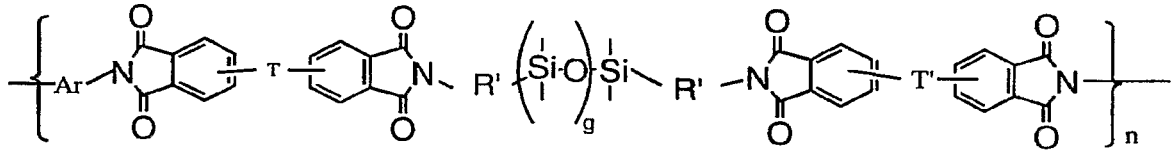
having a value of 1 to about 50, in some other instances g may be about 5 to about 30 and R' is an aryl, alkyl or aryl alky group of having about 2 to about 20 carbon atoms.



(Formula XXII)

Some polyetherimde siloxanes may be formed by reaction of an organic diamine, or mixture of diamines, of formula XIX and the amine-terminated organo siloxane of formula XXII and one or more dianhydrides of formula XVIII. The diamino components may be physically mixed prior to reaction with the bis-anhydride(s), thus forming a substantially random copolymer. Alternatively block or alternating copolymers may be formed by selective reaction of XIX and XXII with dianhydrides to make polyimide blocks that are subsequently reacted together. In another instance the siloxane used to prepare the polyetherimde copolymer may have anhydride rather than amine functional end groups, for example as described in US Patent 4,404,350.

In one instance the siloxane polyetherimide copolymer can be of formula XXIII wherein T, R' and g are described as above, n has a value of about5 to about 100 and Ar is an aryl or alkyl aryl group having 6 to about 36 carbons.



(Formula XXIII)

In some siloxane polyetherimides the diamine component of the siloxane polyetherimide copolymers may contain about 20 mole% to about 50 mole % of the amine-terminated organo siloxane of formula XXII and about 50 to about 80 mole % of the organic diamine of formula XIX. In some siloxane copolymers, the siloxane

component contains about 25 to about 40 mole % of the amine or anhydride terminated organo siloxane.

C. High Tg Phase Separated Polymer Blends.

Also disclosed herein are phase separated polymer blends comprising a mixture of: a) a poly aryl ether ketone (PAEK) selected from the group comprising: polyaryl ether ketones, polyaryl ketones, polyether ketones and polyether ether ketones; and combinations thereof with, b) a polyetherimide sulfone (PEIS) having greater than or equal to 50 mole% of the linkages containing an aryl sulfone group.

Phase separated means that the PAEK and the PEIS exist in admixture as separate chemical entities that can be distinguished, using standard analytical techniques, for example such as microscopy, differential scanning calorimetry or dynamic mechanical analysis, to show a least two distinct polymeric phases one of which comprises PAEK resin and one of which comprises PEIS resin. In some instances each phase will contain greater than about 80 wt% of the respective resin. In other instances the blends will form separate distinct domains about 0.1 to about 50 micrometers in size, in others cases the domains will be about 0.1 to about 20 micrometers. Domain size refers to the longest linear dimension as shown by microscopy. The phase separated blends may be completely immiscible or may show partial miscibility but must behave such that, at least in the solid state, the blend shows two or more distinct polymeric phases.

The ratio of PAEK to PEIS can be any that results in a blend that has improved properties i.e. better or worse depending on the end use application, than either resin alone. The ratio, in parts by weight, may be 1:99 to 99:1, depending on the end use application, and the desired property to be improved. The range of ratios can also be 15:85 to 85:15 or even 25:75 to 75:25. Depending on the application, the ratio may also be 40:60 to 60:40. The skilled artisan will appreciate that changing the ratios of the PAEK to PEIS can fall to any real number ratio within the recited ranges depending on the desired result.

The properties of the final blend, which can be adjusted by changing the ratios of ingredients, include heat distortion temperature and load bearing capability. For example, in one embodiment the polyetherimide sulfone resin can be present in any amount effective to change, i.e. improve by increasing, the load bearing capability of the PAEK blends over the individual components themselves. In some instances the PAEK can be present in an amount of about 30 to about 70 wt% of the entire mixture while the amount of the PEIS may be about 70 to about 30 wt% wherein the weight percents are with respect to the combined weight of the PAEK and the PEIS.

In some embodiments the phase separated polymer blend will have a heat distortion temperature (HDT) measured using ASTM method D5418, on a 3.2 mm bar at 0.46 Mpa (66 psi) of greater than or equal to about 170 °C. In other instances the HDT at 0.46 MPA (66 psi) will be greater than or equal to 200 °C. In still other instances, load bearing capability of the PAEK – PEIS will be shown in a Vicat temperature, as measured by ASTM method D1525 at 50 newtons (N) of greater than or equal to about 200 °C.

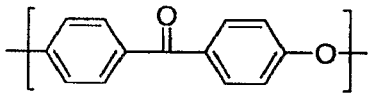
In still other instances load bearing capability of the phase separated polymer blend will be shown by a flexural modulus of greater than or equal to about 200 megapascals (MPa) as measured on a 3.2 mm bar, for example as measured by ASTM method D5418, at 200 °C.

The phase separated polymer blends may be made by mixing in the molten state, an amount of PAEK; with and amount of the PEIS The two components may be mixed by any method known to the skilled artisan that will result in a phase separated blend. Such methods include extrusion, sintering and etc.

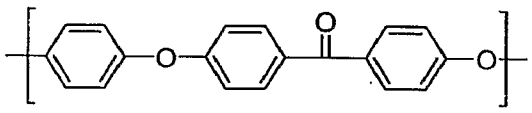
As used herein the term polyaryl ether ketones (PAEK) comprises several polymer types containing aromatic rings, usually phenyl rings, linked primarily by ketone and ether groups in different sequences. Examples of PAEK resins include polyether ketones (PEK), polyether ether ketones (PEEK), polyether ketone ether ketone ketones (PEKEKK) and polyether ketone ketones (PEKK) and copolymers containing such groups as well as blends thereof. The PAEK polymers may comprise monomer

units containing an aromatic ring, usually a phenyl ring, a keto group and an ether group in any sequence. Low levels, for example less than 10 mole %, of addition linking groups may be present as long as they do not fundamentally alter the properties of the PAEK resin

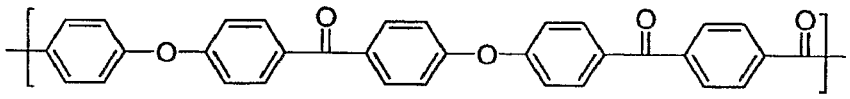
For example, several polyaryl ether ketones which are highly crystalline, with melting points above 300 °C, can be used in the phase separated blends. Examples of these crystalline polyaryl ether ketones are shown in the structures XXVI, XXVII, XXVIII, XXIX, and XXX.



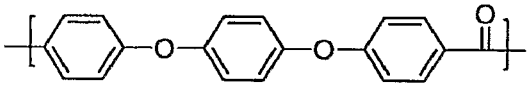
(XXVI)



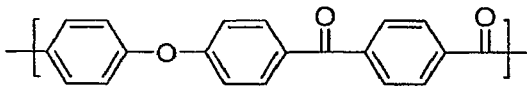
(XXVII)



(XXVIII)

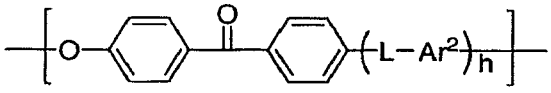


(XXIX)



(XXX)

Other examples of crystalline polyaryl ether ketones which are suitable for use herein can be generically characterized as containing repeating units of the following formula (XXXI):



(XXXI)

wherein Ar^2 is independently a divalent aromatic radical selected from phenylene, biphenylene or naphthylene, L is independently –O-, -C(O)-, -O-Ar-C(O)-, -S-, -SO_2- or a direct bond and h is an integer having a value of 0 to about 10.

The skilled artisan will know that there is a well-developed and substantial body of patent and other literature directed to formation and properties of polyaryl ether ketones. For example, some of the early work, such as US Patent 3,065,205, involves the electrophilic aromatic substitution (e.g., Friedel-Crafts catalyzed) reaction of aromatic diacyl halides with unsubstituted aromatic compounds such as diphenyl ether. The evolution of this class was achieved in US Patent 4,175,175 which shows that a broad range of resins can be formed, for example, by the nucleophilic aromatic substitution reaction of an activated aromatic dihalide and an aromatic diol or salt thereof.

One such method of preparing a poly aryl ketone comprises heating a substantially equimolar mixture of a bisphenol, often reacted as its bis-phenolate salt, and a dihalobenzoid compound or, in other cases, a halophenol compound. In other instances mixtures of these compounds may be used. For example hydroquinone can be reacted with a dihalo aryl ketone, such a dichloro benzophenone or difluoro benzophenone to form a poly aryl ether ketone. In other cases a dihydroxy aryl ketone, such as dihydroxy benzophenone can be polymerized with aryl dihalides such as dichloro benzene to form PAEK resins. In still other instances dihydroxy aryl

ethers, such as dihydroxy diphenyl ether can be reacted with dihalo aryl ketones, such a difluoro benzophenone. In other variations dihydroxy compounds with no ether linkages, such as or dihydroxy biphenyl or hydroquinone may be reacted with dihalo compounds which may have both ether and ketone linkages, for instance bis-(dichloro phenyl) benzophenone. In other instances diaryl ether carboxylic acids, or carboxylic acid halides can be polymerized to form poly aryl ether ketones. Examples of such compounds are diphenylether carboxylic acid, diphenyl ether carboxylic acid chloride, phenoxy-phenoxy benzoic acid, or mixtures thereof. In still other instances dicarboxylic acids or dicarboxylic acid halides can be condensed with diaryl ethers, for instance iso or tere phthaloyl chlorides (or mixtures thereof) can be reacted with diphenyl ether, to form PAEK resins.

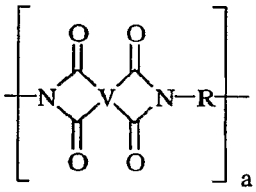
The process is described in, for example, US Patent 4,176,222. The process comprises heating in the temperature range of 100 to 400 °C, (i) a substantially equimolar mixture of: (a) a bisphenol; and, (b.i) a dihalobenzenoid compound, and/or (b.ii) a halophenol, in which in the dihalobenzenoid compound or halophenol, the halogen atoms are activated by –C=O- groups ortho or para thereto, with a mixture of sodium carbonate or bicarbonate and a second alkali metal carbonate or bicarbonate, the alkali metal of said second alkali metal carbonate or bicarbonate having a higher atomic number than that of sodium, the amount of said second alkali metal carbonate or bicarbonate being such that there are 0.001 to 0.2 gram atoms of said alkali metal of higher atomic number per gram atom of sodium, the total amount of alkali metal carbonate or bicarbonate being such that there is at least one alkali metal atom for each phenol group present, and thereafter separating the polymer from the alkali metal halide.

Yet other poly aryl ether ketones may also be prepared according to the process as described in, for example, US Patent 4,396,755. In such processes, reactants such as: (a) a dicarboxylic acid; (b) a divalent aromatic radical and a mono aromatic dicarboxylic acid and, (c) combinations of (a) and (b), are reacted in the presence of a fluoro alkane sulfonic acid, particularly trifluoromethane sulfonic acid.

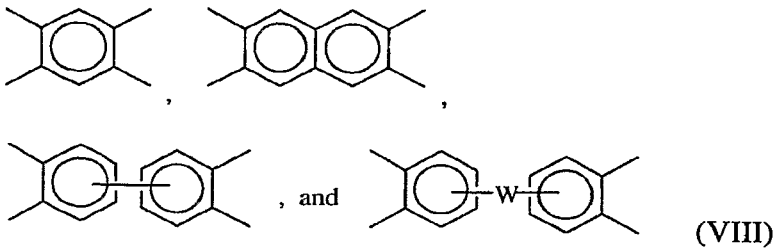
Additional polyaryl ether ketones may be prepared according to the process as described in, for example, US Patent 4,398,020 wherein aromatic diacyl compounds are polymerized with an aromatic compound and a mono acyl halide.

The polyaryl ether ketones may have a reduced viscosity of greater than or equal to about 0.4 to about 5.0 dl/g, as measured in concentrated sulfuric acid at 25 °C. PAEK weight average molecular weight (Mw) may be about 5,000 to about 150,000 g/mole. In other instances Mw may be about 10,000 to about 80,000 g/mole.

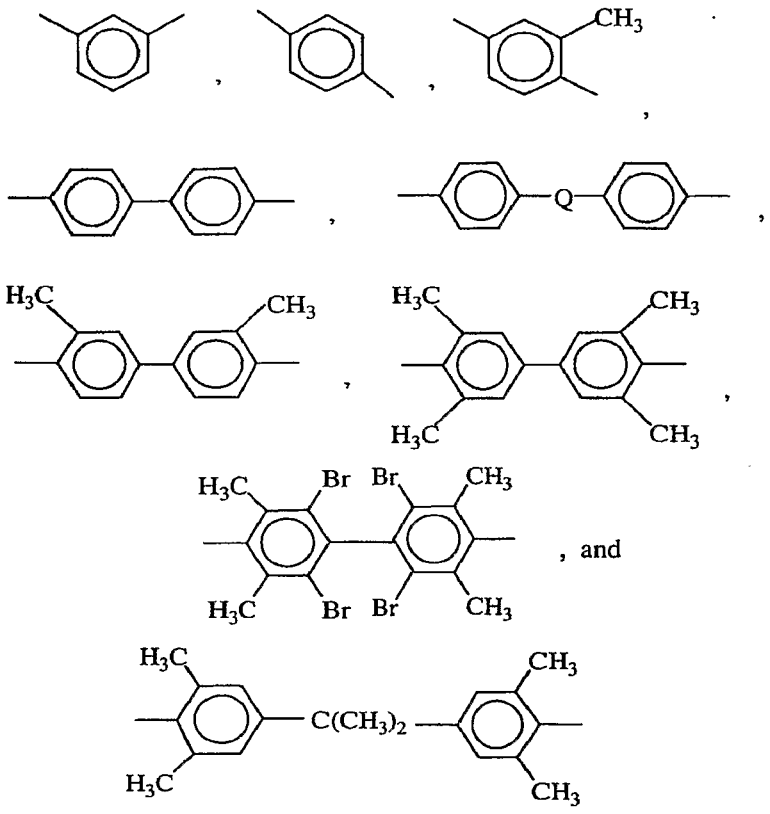
The second resin component is a polyetherimide sulfone (PEIS) resin. As used herein the PEIS comprises structural units having the general formula (VII) wherein greater than or equal to about 50 mole% of the polymer linkages have an aryl sulfone group and


(VII)

wherein a is more than 1, typically about 10 to about 1000 or more, or, more specifically, about 10 to about 500; and V is a tetravalent linker without limitation, as long as the linker does not impede synthesis or use of the polysulfone etherimide. Suitable linkers include but are not limited to: (a) substituted or unsubstituted, saturated, unsaturated or aromatic monocyclic or polycyclic groups having about 5 to about 50 carbon atoms; (b) substituted or unsubstituted, linear or branched, saturated or unsaturated alkyl groups having 1 to about 30 carbon atoms; or (c) combinations thereof. Preferred linkers include but are not limited to tetravalent aromatic radicals of formula (VIII), such as,


(VIII)

wherein W is in some embodiments a divalent group selected from the group consisting of $-SO_2-$, -O-, -S-, -C(O)-, $C_yH_{2y}-$ (y being an integer having a value of 1 to 5), and halogenated derivatives thereof, including perfluoroalkylene groups, or a group of the formula -O-D-O-. The group D may comprise the residue of bisphenol compounds. For example, D may be any of the molecules shown in formula IX.



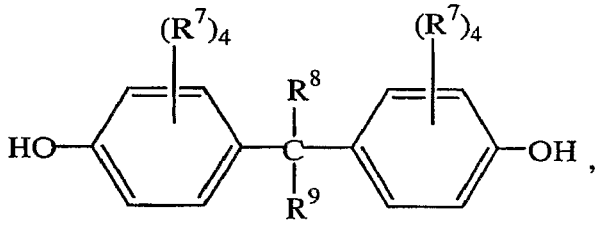
(IX)

The divalent bonds of the -W- or the -O-D-O- group may be in the 3,3', 3,4', 4,3', or the 4,4' positions. Mixtures of the aforesaid compounds may also be used. Groups free of benzylic protons are often preferred for superior melt stability. Groups where W is $-SO_2-$ are of specific note as they are one method of introducing aryl sulfone linkages into the polysulfone etherimide resins.

As used herein the term "polymer linkage" or "a polymer linkage" is defined as the reaction product of at least two monomers which form the polymer, wherein at least one of the monomers is a dianhydride, or chemical equivalent, and wherein the second monomer is at least one diamine, or chemical equivalent. The polymer is

comprised on 100 mole % of such linkages. A polymer which has 50 mole % aryl sulfone linkages, for example, will have half of its linkages (on a molar basis) comprising dianhydride or diamine derived linkages with at least one aryl sulfone group.

Suitable dihydroxy-substituted aromatic hydrocarbons used as precursors to the –O-D-O- group also include those of the formula (X):



(X);

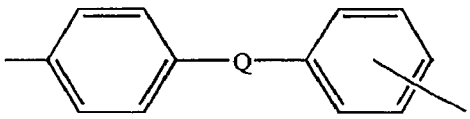
where each R^7 is independently hydrogen, chlorine, bromine, alkoxy, aryloxy or a C_{1-30} monovalent hydrocarbon or hydrocarbonoxy group, and R^8 and R^9 are independently hydrogen, aryl, alkyl fluoro groups or C_{1-30} hydrocarbon groups.

Dihydroxy-substituted aromatic hydrocarbons that may be used as precursors to the –O-D-O- group include those disclosed by name or formula in US Patents 2,991,273, 2,999,835, 3,028,365, 3,148,172, 3,153,008, 3,271,367, 3,271,368, and 4,217,438. Specific examples of dihydroxy-substituted aromatic hydrocarbons which can be used include, but are not limited to, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl) ether, bis(4-hydroxyphenyl)sulfoxide, 1,4-dihydroxybenzene, 4,4'-oxydiphenol, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol; 4,4'-bis(3,5-dimethyl)diphenol, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane; 4,4-bis(4-hydroxyphenyl)heptane; 2,4´-dihydroxydiphenylmethane; bis(2-hydroxyphenyl)methane; bis(4-hydroxyphenyl)methane; bis(4-hydroxy-5-nitrophenyl)methane; bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 1,2-bis(4-hydroxyphenyl)ethane; 1,1-bis(4-hydroxy-2-chlorophenyl)ethane; 2,2-bis(3-phenyl-4-hydroxyphenyl)propane; 2,2-bis(4-hydroxy-3-methylphenyl)propane; 2,2-bis(4-hydroxy-3-ethylphenyl)propane; 2,2-bis(4-hydroxy-3-isopropylphenyl)propane; 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane;

3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane; bis(4-hydroxyphenyl)cyclohexylmethane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; 2,4'-dihydroxyphenyl sulfone; dihydroxy naphthalene; 2,6-dihydroxy naphthalene; hydroquinone; resorcinol; C_{1-3} alkyl-substituted resorcinols; methyl resorcinol, 1,4-dihydroxy-3-methylbenzene; 2,2-bis(4-hydroxyphenyl)butane; 2,2-bis(4-hydroxyphenyl)-2-methylbutane; 1,1-bis(4-hydroxyphenyl)cyclohexane; 4,4'-dihydroxydiphenyl; 2-(3-methyl-4-hydroxyphenyl-2-(4-hydroxyphenyl)propane; 2-(3,5-dimethyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3-methyl-4-hydroxyphenyl)-2-(3,5-dimethyl-4-hydroxyphenyl)propane; bis(3,5-dimethylphenyl-4-hydroxyphenyl)methane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)ethane; 2,2-bis(3,5-dimethylphenyl-4-hydroxyphenyl)propane; 2,4-bis(3,5-dimethylphenyl-4-hydroxyphenyl)-2-methylbutane; 3,3-bis(3,5-dimethylphenyl-4-hydroxyphenyl)pentane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)cyclopentane; 1,1-bis(3,5-dimethylphenyl-4-hydroxyphenyl)cyclohexane; bis(3,5-dimethyl-4-hydroxyphenyl) sulfoxide, bis(3,5-dimethyl-4-hydroxyphenyl) sulfone and bis(3,5-dimethylphenyl-4-hydroxyphenyl)sulfide. Mixtures comprising any of the foregoing dihydroxy-substituted aromatic hydrocarbons may also be employed.

In a particular embodiment the dihydroxy-substituted aromatic hydrocarbon comprising bisphenols with sulfone linkages are of note as this is another route to introducing aryl sulfone linkages into the polysulfone etherimide resin. In other instances bisphenol compounds free of benzylic protons may be preferred to make polyetherimide sulfones with superior melt stability.

In Formula (VII) the R group is the residue of a diamino compound, or chemical equivalent, that includes but is not limited to substituted or unsubstituted divalent organic radicals such as: (a) aromatic hydrocarbon radicals having about 6 to about 24 carbon atoms and halogenated derivatives thereof; (b) straight or branched chain alkylene radicals having about 2 to about 20 carbon atoms; (c) cycloalkylene radicals having about 3 to about 24 carbon atoms, or (d) divalent radicals of the general formula (XI)



(XI)

wherein Q includes but is not limited to a divalent group selected from the group consisting of $-SO_2-$, -O-, -S-, -C(O)-, $C_yH_{2y}-$ (y being an integer having a value of 1 to about 5), and halogenated derivatives thereof, including perfluoroalkylene groups. In particular embodiments R is essentially free of benzylic hydrogens. The presence of benzylic protons can be deduced from the chemical structure.

In some particular embodiments suitable aromatic diamines comprise meta-phenylenediamine; para-phenylenediamine; mixtures of meta- and para-phenylenediamine; isomeric 2-methyl- and 5-methyl-4,6-diethyl-1,3-phenylene-diamines or their mixtures; bis(4-aminophenyl)-2,2-propane; bis(2-chloro-4-amino-3,5-diethylphenyl)methane, 4,4'-diaminodiphenyl, 3,4'-diaminodiphenyl, 4,4'-diaminodiphenyl ether (sometimes referred to as 4,4'-oxydianiline); 3,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl sulfide; 3,4'-diaminodiphenyl sulfide; 4,4'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 4,4'-diaminodiphenylmethane (commonly named 4,4'-methylenedianiline); 4,4'-bis(4-aminophenoxy)biphenyl, 4,4'-bis(3-aminophenoxy)biphenyl, 1,5-diaminonaphthalene; 3,3-dimethylbenzidine; 3,3-dimethoxybenzidine; benzidine; m-xylylenediamine; bis(aminophenoxy)fluorene, bis(aminophenoxy)benzene, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, bis(aminophenoxy)phenyl sulfone, bis(4-(4-aminophenoxy)phenyl) sulfone, bis(4-(3-aminophenoxy)phenyl) sulfone, diaminobenzanilide, 3,3'-diaminobenzophenone, 4,4'-diaminobenzophenone, 2,2'-bis(4-(4-aminophenoxy)phenyl)propane, 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane, 4,4'-bis(aminophenyl)hexafluoropropane, 1,3-diamino-4-isopropylbenzene; 1,2-bis(3-aminophenoxy)ethane; 2,4-bis(beta-amino-t-butyl)toluene; bis(p-beta-methyl-o-aminophenyl)benzene; bis(p-beta-amino-t-butylphenyl)ether and 2,4-toluenediamine. Mixtures of two or more diamines may also be employed. Diamino diphenyl sulfone

(DDS), bis(aminophenoxy phenyl) sulfones (BAPS) and mixtures thereof are preferred aromatic diamines.

Thermoplastic polysulfone etherimides described herein can be derived from reactants comprising one or more aromatic diamines or their chemically equivalent derivatives and one or more aromatic tetracarboxylic acid cyclic dianhydrides (sometimes referred to hereinafter as aromatic dianhydrides), aromatic tetracarboxylic acids, or their derivatives capable of forming cyclic anhydrides or the thermal/catalytic rearrangement of preformed polyisoimides. In addition, at least a portion of one or the other of, or at least a portion of each of, the reactants comprising aromatic diamines and aromatic dianhydrides comprises an aryl sulfone linkage such that at least 50 mole % of the resultant polymer linkages contain at least one aryl sulfone group. In a particular embodiment all of one or the other of, or, each of, the reactants comprising aromatic diamines and aromatic dianhydrides having at least one sulfone linkage. The reactants polymerize to form polymers comprising cyclic imide linkages and sulfone linkages.

Illustrative examples of aromatic dianhydrides include:

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfone dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride, and mixtures thereof.

Other useful aromatic dianhydrides comprise:

2,2-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(3,4-dicarboxyphenoxy)benzophenone dianhydride;

2,2-bis([4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl ether dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4,4'-bis(2,3-dicarboxyphenoxy)benzophenone dianhydride;

2-[4-(3,4-dicarboxyphenoxy)phenyl]-2-[4-(2,3-dicarboxyphenoxy)phenyl]propane dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl ether dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride;

4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)benzophenone dianhydride;

1,4,5,8-naphthalenetetracarboxylic acid dianhydride;

3,4,3',4'-benzophenonetetracarboxylic acid dianhydride;

2,3,3',4'-benzophenonetetracarboxylic acid dianhydride;

3,4,3',4'-oxydiphthalic anhydride; 2,3,3',4'-oxydiphthalic anhydride;

3,3',4,4'-biphenyltetracarboxylic acid dianhydride;

2,3,3',4'-biphenyltetracarboxylic acid dianhydride;

2,3,2',3'-biphenyltetracarboxylic acid dianhydride; pyromellitic dianhydride; 3,4,3',4'-diphenylsulfonetetracarboxylic acid dianhydride;

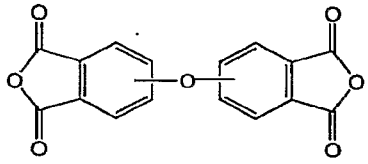
2,3,3',4'-diphenylsulfonetetracarboxylic acid dianhydride;

1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride; and,

2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride. Polysulfone etherimides with structural units derived from mixtures comprising two or more dianhydrides are also contemplated.

In other instances, the polysulfone etherimides have greater than or equal to about 50 mole % imide linkages derived from an aromatic ether anhydride that is an oxydiphthalic anhydride, in an alternative embodiment, about 60 mole % to about 100 mole % oxydiphthalic anhydride derived imide linkages. In an alternative embodiment, about 70 mole % to about 99 mole % of the imide linkages are derived from oxydiphthalic anhydride or chemical equivalent.

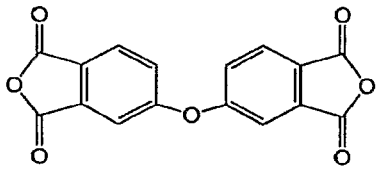
The term "oxydiphthalic anhydride" means the oxydiphthalic anhydride of the formula (XII)



(XII)

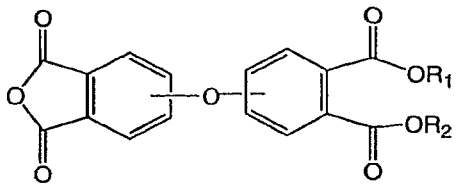
and derivatives thereof as further defined below.

The oxydiphthalic anhydrides of formula (XII) includes 4,4'-oxybisphthalic anhydride, 3,4'-oxybisphthalic anhydride, 3,3'-oxybisphthalic anhydride, and any mixtures thereof. For example, the polysulfone etherimide containing greater than or equal to about 50 mole % imide linkages derived from oxydiphthalic anhydride may be derived from 4,4'-oxybisphthalic anhydride structural units of formula (XIII)



(XIII)

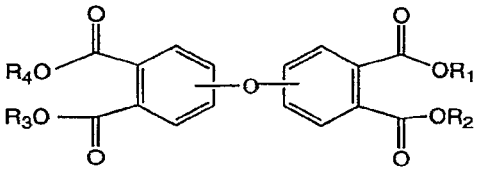
As mentioned above, derivatives of oxydiphthalic anhydrides may be employed to make polysulfone etherimides. Examples of a derivatized anhydride group which can function as a chemical equivalent for the oxydiphthalic anhydride in imide forming reactions, includes oxydiphthalic anhydride derivatives of the formula (XIV)



(XIV)

wherein R_1 and R_2 of formula VII can be any of the following: hydrogen; an alkyl group; an aryl group. R_1 and R_2 can be the same or different to produce an oxydiphthalic anhydride acid, an oxydiphthalic anhydride ester, and an oxydiphthalic anhydride acid ester.

The polysulfone etherimides herein may include imide linkages derived from oxydiphthalic anhydride derivatives which have two derivatized anhydride groups, such as for example, where the oxy diphthalic anhydride derivative is of the formula (XV)



(XV)

wherein R_1, R_2, R_3 and R_4 of formula (XV) can be any of the following: hydrogen; an alkyl group, an aryl group. R_1, R_2, R_3, and R_4 can be the same or different to produce an oxydiphthalic acid, an oxydiphthalic ester, and an oxydiphthalic acid ester.

Copolymers of polysulfone etherimides which include structural units derived from imidization reactions of mixtures of the oxydiphthalic anhydrides listed above having two, three, or more different dianhydrides, and a more or less equal molar amount of an organic diamine with a flexible linkage, are also contemplated. In addition, copolymers having greater than or equal to about 50 mole % imide linkages derived from oxy diphthalic anhydrides defined above, which includes derivatives thereof, and up to about 50 mole % of alternative dianhydrides distinct from oxydiphthalic anhydride are also contemplated. That is, in some instances it will be desirable to make copolymers that in addition to having greater than or equal to about 50 mole % linkages derived from oxydiphthalic anhydride, will also include imide linkages

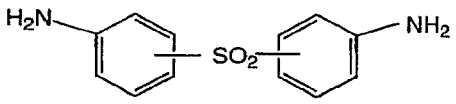
derived from aromatic dianhydrides different than oxydiphthalic anhydrides such as, for example, bisphenol A dianhydride (BPADA), disulfone dianhydride, benzophenone dianhydride, bis (carbophenoxy phenyl) hexafluoro propane dianhydride, bisphenol dianhydride, pyromellitic dianhydride (PMDA), biphenyl dianhydride, sulfur dianhydride, sulfo dianhydride and mixtures thereof.

In another embodiment, the dianhydride, as defined above, reacts with an aryl diamine that has a sulfone linkage. In one embodiment the polysulfone etherimide includes structural units that are derived from an aryl diamino sulfone of the formula (XVI)

$$H_2N—Ar—SO_2—Ar—NH_2 \quad \text{(XVI)}$$

wherein Ar can be an aryl group species containing a single or multiple rings. Several aryl rings may be linked together, for example through ether linkages, sulfone linkages or more than one sulfone linkages. The aryl rings may also be fused.

In alternative embodiments, the amine groups of the aryl diamino sulfone can be meta or para to the sulfone linkage, for example, as in formula (XVII)



(XVII)

Aromatic diamines include, but are not limited to, for example, diamino diphenyl sulfone (DDS) and bis(aminophenoxy phenyl) sulfones (BAPS). The oxy diphthalic anhydrides described above may be used to form polyimide linkages by reaction with an aryl diamino sulfone to produce polysulfone etherimides.

In some embodiments the polysulfone etherimide resins can be prepared from reaction of an aromatic dianhydride monomer (or aromatic bis(ether anhydride) monomer) with an organic diamine monomer wherein the two monomers are present in essentially equimolar amounts, or wherein one monomer is present in the reaction mixture at no more than about 20% molar excess, and preferably less than about 10% molar excess in relation to the other monomer, or wherein one monomer is present in

the reaction mixture at no more than about 5% molar excess. In other instances the monomers will be present in amounts differing by less than 1% molar excess.

Alkyl primary amines such as methyl amine may be used as chain stoppers. Primary monoamines may also be used to end-cap or chain-stop the polysulfone etherimide, for example, to control molecular weight. In a particular embodiment primary monoamines comprise aromatic primary monoamines, illustrative examples of which comprise aniline, chloroaniline, perfluoromethyl aniline, naphthyl amines and the like. Aromatic primary monoamines may have additional functionality bound to the aromatic ring: such as, but not limited to, aryl groups, alkyl groups, aryl-alkyl groups, sulfone groups, ester groups, amide groups, halogens, halogenated alkyl or aryl groups, alkyl ether groups, aryl ether groups, or aryl keto groups. The attached functionality should not impede the function of the aromatic primary monoamine to control polysulfone etherimide molecular weight. Suitable monoamine compounds are listed in US Patent 6,919,422.

Aromatic dicarboxylic acid anhydrides, that is aromatic groups comprising one cyclic anhydride group, may also be used to control molecular weight in polyimide sulfones. Illustrative examples comprise phthalic anhydride, substituted phthalic anhydrides, such as chlorophthalic anhydride, and the like. Said anhydrides may have additional functionality bound to the aromatic ring, illustrative examples of which comprise those functionalities described above for aromatic primary monoamines.

In some instances polysulfone etherimides with low levels of isoalkylidene linkages may be desirable. It is believed that in some PAEK blends the presence of isoalkylidene linkages may promote miscibility, which could reduce load bearing capability at high temperature and would be undesirable. Miscible PEEK blends with isoalkylidene containing polymer are described, for example, US Patents 5,079,309 and 5,171,796. In some instances low levels of isoalkylidene groups can mean less that 30 mole % of the polysulfone etherimide linkages will contain isoalkylidene groups, in other instances the polysulfone etherimide linkages will contain less than 20 mole % isoalkylidene groups. In still other instances less than 10 mole % isoalkylidene groups will be present in the polysulfone etherimide linkages.

Polysulfone etherimides may have a melt index of about 0.1 to about 10 grams per minute (g/min), as measured by American Society for Testing Materials (ASTM) D1238 at 340-425 °C. In a one embodiment, the polysulfone etherimide resin has a weight average molecular weight (Mw) of about 10,000 to about 150,000 grams per mole (g/mole), as measured by gel permeation chromatography, using a polystyrene standard. In another embodiment the polysulfone etherimide has Mw of 20,000 to 60,000 g/mole. Examples of some polyetherimides are listed in ASTM D5205 "Standard Classification System for Polyetherimide (PEI) Materials".

In some instances, especially where the formation of the film and fiber are desired, the composition should be essentially free of fibrous reinforcement such as glass, carbon, ceramic or metal fibers. Essentially free in some instances means less than 5 wt% of the entire composition. In other cases, the composition should have less than 1wt% fibrous reinforcement present.

In other instances it is useful to have compositions that develop some degree of crystallinity on cooling. This may be more important in articles with high surface area such as fibers and films which will cool of quickly due to their high surface area and may not develop the full crystallinity necessary to get optimal properties. In some instances the formation of crystallinity is reflected in the crystallization temperature (Tc), which can be measured by a methods such as differential scanning calorimetry (DSC), for example, ASTM method D3418. The temperature of the maximum rate of crystallization may be measured as the Tc. In some instances, for example at a cooling rate of 80 °C/min., it may be desirable to have a Tc of greater than or equal to about 240 °C. In other instances, for example a slower cooling rate of 20 °C/min., a crystallization temperature of greater than or equal to about 280 °C may be desired.

In some instances the composition will have at least two distinct glass transition temperatures (Tg), a first Tg from the PAEK resin, or a partially miscible PAEK blend, and a second Tg associated with the polysulfone etherimide resin, or mixture where such resin predominates. These glass transition temperatures (Tgs) can be measured by any conventional method such as DSC or dynamic mechanical analysis (DMA). In some instances the first Tg can be about 120 to about 200 °C and the

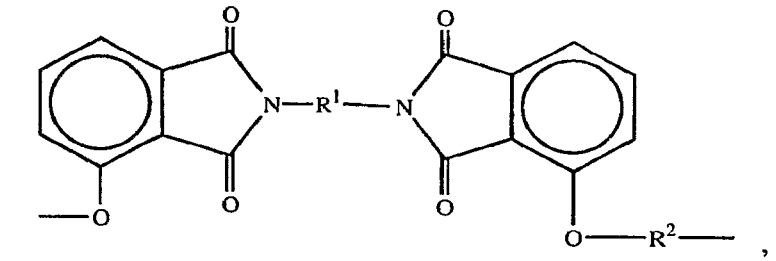
second Tg can be about 240 to about 350 °C. In other instances it may be useful to have an even higher second Tg, about 280 to about 350 °C. In some instances, depending on the specific resins, molecular weights and composition of the blend, the Tgs may be distinct or the transitions may partially overlap.

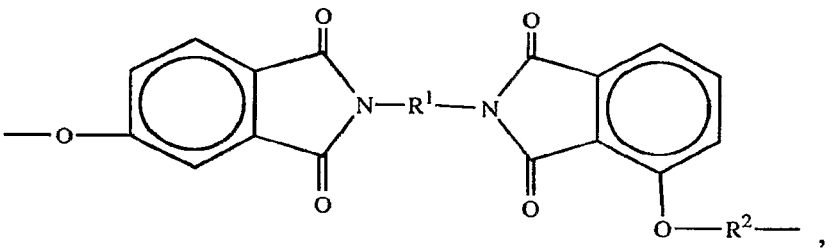
In another embodiment the polysulfone etherimide PEAK blends will have melt viscosity of about 200 Pascal-seconds to about 10,000 Pascal-seconds (Pa-s) at 380°C as measured by ASTM method D3835 using a capillary rheometer with a shear rate of 100 to 10000 1/sec. Resin blends having a melt viscosity of about 200 Pascal-seconds to about 10,000 Pascal-seconds at 380°C will allow the composition to be more readily formed into articles using melt processing techniques. In other instances a lower melt viscosity of about 200 to about 5,000 Pa-s will be useful.

Another aspect of melt processing, especially at the high temperature needed for the PAEK-polysulfone etherimide compositions described herein, is that the melt viscosity of the composition not undergo excessive change during the molding or extrusion process. One method to measure melt stability is to examine the change in viscosity vs. time at a processing temperature, for example 380°C using a parallel plate rheometer. In some instances greater than or equal to about 50% of the initial viscosity should be retained after being held at temperature for greater than or equal to about 10 minutes. In other instances the melt viscosity change should be less than about 35% of the initial value for at least about 10 minutes. The initial melt viscosity values can be measured from 1 to 5 minutes after the composition has melted and equilibrated. It is common to wait 1-5 minutes after heat is applied to the sample before measuring (recording) viscosity to ensure the sample is fully melted and equilibrated. Suitable methods for measuring melt viscosity vs. time are, for example, ASTM method D4440. Note that melt viscosity can be reported in poise (P) or Pascal seconds (Pa-s); 1Pa-s = 10P.

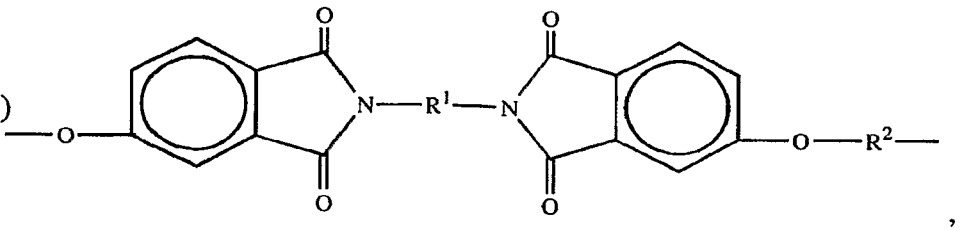
D. Co-Polyetherimides

Useful polymers can also include co-polymers of a copolyetherimide having a glass transition temperature greater than or equal to about 218°C, said copolyetherimide comprising structural units of the formulas (I) and (II):

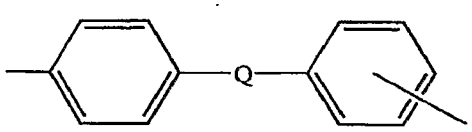
(I) 

(II) 

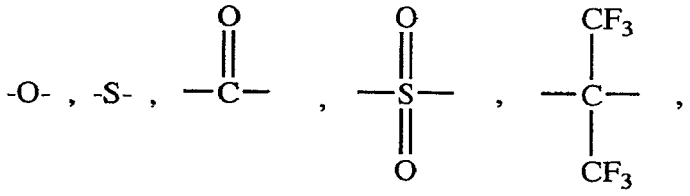
and optionally structural units of the formula (III):

(III) 

wherein R^1 comprises an unsubstituted C_{6-22} divalent aromatic hydrocarbon or a substituted C_{6-22} divalent aromatic hydrocarbon comprising halogen or alkyl substituents or mixtures of said substituents; or a divalent radical of the general formula (IV):

(IV) 

group wherein the unassigned positional isomer about the aromatic ring is either meta or para to Q, and Q is a covalent bond, a $-C(CH_3)_2$ or a member selected from the consisting of formulas (V):

(V) 

and an alkylene or alkylidene group of the formula C_yH_{2y}, wherein y is an integer having a value of 1 to about 5, and R^2 is a divalent aromatic radical; the weight ratio of units of formula (I) to those of formula (II) being in the range of about 99.9:0.1 and about 25:75. Co-polymers having these elements are more fully discussed in US Patent 6,849,706, issued February 1, 2005, in the names of Brunelle et al., titled "COPOLYETHERIMIDES", herein incorporated by reference in its entirety as though set forth in full.

The polymer blends used in articles according to the present invention can be blended with the aforementioned ingredients by a variety of methods involving intimate admixing of the materials with any additional additives desired in the formulation. A preferred procedure includes melt blending, although solution blending is also possible. Because of the availability of melt blending equipment in commercial polymer processing facilities, melt processing methods are generally preferred. Illustrative examples of equipment used in such melt processing methods include: co-rotating and counter-rotating extruders, single screw extruders, co-kneaders, disc-pack processors and various other types of extrusion equipment. The temperature of the melt in the present process is preferably minimized in order to avoid excessive degradation of the resins In some embodiments the melt processed composition exits processing equipment such as an extruder through small exit holes in a die, and the resulting strands of molten resin are cooled by passing the strands through a water bath. The cooled strands can be chopped and/or molded into any convenient shape, i.e. pellets, for packaging, further handling or ease of end use production.

The blends discussed herein can be prepared by a variety of melt blending techniques. Use of a vacuum vented single or twin screw extruder with a good mixing screw is preferred. In general, the melt processing temperature at which such an extruder should be run is about 100° to about 150° C higher than the Tg of the thermoplastic. The mixture of ingredients may all be fed together at the throat of the extruder using individual feeders or as a mixture. In some cases, for instance in blends of two or more resins, it may be advantageous to first extrude a portion of the ingredients in a first extrusion and then add the remainder of the mixture in a second extrusion. It may be useful to first precompound the colorants into a concentrate which is subsequently mixed with the remainder of the resin composition. In other situations it may be beneficial to add portions of the mixture further down stream from the extruder throat. After extrusion the polymer melt can be stranded and cooled prior to chopping or dicing into pellets of appropriate size for the next manufacturing step. Preferred pellets are about 1/16 to 1/8 inch long, but the skilled artisan will appreciate that any pellet size will do. The pelletized thermoplastic resins are then dried to remove water and molded into the articles of the invention. Drying at about 135° to about 150°C for about 4 to about 8 hours is preferred, but drying times will vary with resin type. Injection molding is preferred using suitable temperature, pressures, and clamping to produce articles with a glossy surface. Melt temperatures for molding will be about 100° to about 200° C above the T_g of the resin. Oil heated molds are preferred for higher Tg resins, mold temperatures can range from about 50° to about 175° C with temperatures of about 120° to about 175° C preferred. The skilled artisan will appreciate the many variations of these compounding and molding conditions can be employed to make the foams of the present invention.

EXAMPLES

Without further elaboration, it is believed that the skilled artisan can, using the description herein, make and use the present invention. The following examples are included to provide additional guidance to those skilled in the art of practicing the claimed invention. These examples are provided as representative of the work and contribute to the teaching of the present invention. Accordingly, these examples are

not intended to limit the scope of the present invention in any way. Unless otherwise specified below, all parts are by weight.

EXAMPLE I

Materials

PCE is BPA co polycarbonate ester containing about 60 wt % of a 1:1 mixture iso and tere phthalate ester groups and the remainder BPA carbonate groups, , Mw ~ 28,300 and has Tg of about 175°C.

PSEI-1 is a polysulfone etherimide made by reaction of 4,4'-oxydiphthalic anhydride (ODPA) with about an equal molar amount of 4,4'-diamino diphenyl sulfone (DDS), Mw ~33,000 and has a Tg of about 310° C.

PSEI-2 is a polysulfone etherimide copolymer made by reaction of a mixture of about 80 mole % 4,4'-oxydiphthalic anhydride (ODPA) and about 20 mole % of bisphenol–A dianhydride (BPADA) with about an equal molar amount of 4,4'-diamino diphenyl sulfone (DDS), Mw ~ 28,000 and has a Tg of about 280° C.

PSEI-3 is a polysulfone etherimide made from reaction of bisphenol–A dianhydride (BPADA) with about an equal molar amount of 4,4'-diamino diphenyl sulfone (DDS), Mw ~ 34,000 and has a Tg of about 247° C.

PSEI-4 is a polysulfone etherimide made from reaction of bisphenol-A disodium salt with a equal molar amount of 1H-Isoindole-1,3(2H)-dione, 2,2'-(sulfonyldi-4,1-phenylene)bis[4-chloro- (9CI) Mw ~50,000 and has a Tg of about 265° C.

Inventive formulations 1-9 are prepared using the compositions specified in Table 1. Amounts of all components are expressed as parts per hundred parts resin by weight (phr), where the total resin weight includes stabilizers, if present. Polycarbonate ester (PCE) copolymer is prepared in a two-phase (methylene chloride/water) reaction of isophthaloyl and terephthaloyl diacid chloride with bisphenol A in the presence of base and a triethylamine phase transfer catalyst. Synthetic details for this type of synthesis can be found in, for example, U.S. Pat. No. 5,521,258 at column 13, lines

15-45. The resulting polyester carbonate copolymer has 60% ester units (as a 1:1 weight/weight mixture of isophthalate and terephthalate units) and 40% carbonate units based on bisphenol A. Ingredients as specified in Table 1 are mixed together in a paint shaker and extruded at 575-640° F at 80-90 rpm on a 2.5 inch vacuum vented single screw extruder. The resulting blends are pelletized and the pellets are dried for 4 hours at 275° F prior to injection molding into 5 X 7 X 1/8 inch plaques. The molding machine is set for a 675° F melt temperature and a 275° F mold temperature.

Table 1

Formulations	1	2	3	4	5	6	7	8	9
PCE	60	50	50	30	40	60	70	45	65
PSEI-3				70	60	40	30		
PSEI-2		50						55	
PSEI-1	40		50						35

EXAMPLE II

A concentrated foamable resin is formed by mechanically blending 20 parts by weight of 5-phenyl-3,6-dihydro-1,3,4-oxadiazine-2-one (PDOX) and 80 parts by weight of each of formulations 1-9 which have been previously ground to 20 mesh or less. The foamable resin has an intrinsic viscosity of 0.38-0.42 in chloroform. The resin is predried for 8 hours at 121°C.

The premix is placed in an extruder with a barrel temperature of 188-199° C. The extruder usees a low sheer "compounding screw" to minimize frictional heating. The resulting stock temperature is 199-216°C. The extruded strand is water quenched and then chopped. The amount of PDOX present is determined by thermogravimetric analysis.

The concentrate is then blended with predried resin, 10% and 30% glass-filled resin at a level of 2% by weight. The resulting blends are then extruded on a foam molding press (Reed) with a barrel profile range of 306-370°C. The mold is set at 93°C. Standard tensile and flexural specimens (63.5 mm thick) are molded.

EXAMPLE III

Formulation 10-11

Materials

Resorcinol ester polycarbonate (ITR) resin used in these formulations is a polymer made from the condensation of a 1:1 mixture of iso and terephthaloyl chloride with resorcinol, bisphenol A (BPA) and phosgene. The ITR polymers are named by the approximate mole ratio of ester linkages to carbonate linkages. ITR9010 has about 82 mole % resorcinol ester linkages, 8 mole % resorcinol carbonate linkages and about 10 mole % BPA carbonate linkages. Tg = 131°C

PEI = ULTEM 1000 polyetherimide, made by reaction of bisphenol A dianhydride with about an equal molar amount of m-phenylene diamine, from GE Plastics.

PEI-Siloxane is a polyetherimide dimethyl siloxane copolymer made from the imidization reaction of m-phenylene diamine, BPA-dianhydride and a bis-aminopropyl functional methyl silicone containing on average about 10 silicone atoms. It has about 34 wt% siloxane content and a Mn of about 24,000 as measured by gel permeation chromatography.

PC is BPA polycarbonate, LEXAN 130 from GE Plastics.

Blends are prepared by extrusion of mixtures of resorcinol based polyester carbonate resin with polyetherimide and silicone polyimide copolymer resin in a 2.5 inch single screw, vacuum vented extruder. Compositions are listed in wt% of the total composition except where noted otherwise. The extruder is set at about 285 to 340 °C. The blends were run at about 90 rpm under vacuum. The extrudate is cooled, pelletized and dried at 120 °C.

Table 2

Formulations	10	11
PEI	76	76
ITR9010	10	20
PEI-Siloxane	4	4
PC	10	0
TiO_2	3	3

Formulations 10 and 11 are dried overnight at a temperature of 121°C. After the resins are sufficiently dry, PDOX is dry blended with the resin at a 0.5% by weight level. This premix is molded into a sheet using a foam molding machine (Reed). The temperature profile was in the range of 306-343°C.

EXAMPLE IV

Blends 12-18 are made using the same process for making blends described for the previous example.

Table 3

Formulations	12	13	14	15	16	17	18
PEI	56.5	78.0	63.0	48.0	69.5	46.0	76.0
ITR9010	42.5	20.0	35.0	50.0	27.5	50.0	20.0
PEI-Siloxane	1.0	2.0	2.0	2.0	3.0	4.0	4.0

All blends 3 phr TiO2 & 0.1 phr triaryl phosphite

99.5 parts by weight of the each of formulations 12-18 is dry blended with 0.5 parts the blowing agent, were 5PT (5-phenyl tetrazole) available as Expandex 150 (the calcium salt of 5-phenyl tetrazole) Olin Chemicals of Stamford, Conn and Expandex 175 (the barium salt of 5-phenyl tetrazole). These blowing agents are sold by Olin Chemicals of Stamford, Conn. The resulting blend is then extruded and formed into a sheet.

EXAMPLE V

Blends 19-25 are made using the same process for making blends described for the previous example.

Table 4

Formulations	19	20	21	22	23	24	25
PEI	67.5	67.5	68	58	19.15	18.40	17.65
ITR9010	30.0	30.0	20	30	80.0	80.0	80.0
PEI-Siloxane	2.5	2.5	2	2	0.75	1.50	2.25
PC			10	10			
Triaryl Phosphite					0.1	0.1	0.1
TiO_2	0.0	3.0	3	3			

and Expandex 175 (the barium salt of 5-phenyl tetrazole). These blowing agents are sold by Olin Chemicals of Stamford, Conn. Each sample was prepared by dry blending 0.5 parts by weight of the blowing agent with 99.5 parts by weight of the resin.

EXAMPLE VI

Formulations 26-31 are made using the same process for making blends described for the previous example.

Table 5

Examples	26	27	28	29	30	31
PEI	49.15	48.40	47.65	79.15	78.40	77.70
ITR 9010	50.0	50.0	50.0	20.0	20.0	20.0
PEI Siloxane	0.75	1.50	2.25	0.75	1.50	2.25
Triaryl Phosphite	0.1	0.1	0.1	0.1	0.1	0.1

Pellets comprising one of each of formulations 26-31 are added to a reactor and suspended in an aqueous 0.8% polyvinyl alcohol solution. The suspension is charged with acetone and the temperature is increased to 95°C and held for one hour. The temperature is then increased to 190° C for four hours which will generate increased pressure within the reactor. The pellets are cooled to room temperature, separated from the PVA solution and washed with water. The resultant pellets have acetone absorbed into them. Expansion of the resultant pellets is carried out in a 210° C oven for four minutes.

EXAMPLE VII

Materials

Resorcinol ester polycarbonate (ITR) resin used in these examples is a polymer made from the condensation of a 1:1 mixture of iso and terephthaloyl chloride with resorcinol, bisphenol A (BPA) and phosgene. The ITR polymers are named by the approximate mole ratio of ester linkages to carbonate linkages. ITR9010 had about 82 mole % resorcinol ester linkages, 8 mole % resorcinol carbonate linkages and about

10 mole % BPA carbonate linkages. Tg = 131°C PEI-Siloxane is a polyetherimide dimethyl siloxane copolymer made from the imidization reaction of m-phenylene diamine, BPA-dianhydride and a bis-aminopropyl functional methyl silicone containing on average about 10 silicone atoms. It has about 34 wt% siloxane content and a Mn of about 24,000 as measured by gel permeation chromatography.

PSu is a polysulfone made from reaction of bisphenol A and dichloro diphenyl sulfone, and is sold as UDEL1700 form Solvay Co.

PES is a polyether sulfone made from reaction of dihydroxy phenyl sulfone and dichloro diphenyl sulfone, and is sold as ULTRASON E from BASF Co.

Note that blends according to this example had 3 parts per hundred (phr) titanium dioxide (TiO_2) added during compounding. Blends are prepared by extrusion of mixtures of resorcinol based polyester carbonate resin with polysulfone or polyether sulfone and a silicone polyimide copolymer resin in a 2.5 inch single screw, vacuum vented extruder. Compositions are listed in wt% of the total composition except where noted otherwise. The extruder is set at about 285 to 340 °C. The blends are run at about 90 rpm under vacuum. The extrudate is cooled, pelletized and dried at 120 °C.

Table 6

Formulations	32	33	34
Psu	62.5	31.25	62.5
PES	0	31.25	0
PEI Siloxane	2.5	2.5	2.5
ITR9010	35	35	35

Expanded thermoplastic compositions is produced by charging a pressure reactors with acetone and one of each of formulations 32-34. Each reactor is placed in a 180° C oven for four hours after which the pressure is immediately released and the reactor is quenched to prevent collapsing of the foam.

EXAMPLE VIII

Formulations 35 and 36 in table 7 show blends of PSu or PES with a higher content (60 wt%) of the resorcinol ester polycarbonate copolymer. These blends are made according to the process described in the previous example.

Table 7

Formulations	35	36
PSu	37.5	0
PES	0	37.5
PEI Siloxane	2.5	2.5
ITR9010	60	60

* blends had 3 phr TiO2

Twp pre-mixes are formed by mechanically blending 20 parts by weight of 5-phenyl-3,6-dihydro-1,3,4-oxadiazine-2-one (PDOX) and 80 parts by weight of each of formulations 35 and 36 which are previously ground to 20 mesh or less. The premix is predried for 8 hours at 121° C.

The premixs are placed in extruders with a barrel temperature of 188°-199° C. The extruders use a low sheer "compounding screw" to minimize frictional heating. The stock temperature is 199°-216° C. The extruded strands are water quenched and chopped to form the concentrate.

The concentrate is then blended with each of formulations 35 and 36. The resulting blends are then extruded on a foam molding press.

While the invention has been illustrated and described in typical embodiments, it is not intended to be limited to the details shown, since various modifications and substitutions can be made without departing in any way from the spirit of the present invention. As such, further modifications and equivalents of the invention herein disclosed may occur to persons skilled in the art using no more than routine experimentation, and all such modifications and equivalents are believed to be within the spirit and scope of the invention as defined by the following claims. All aforementioned patents and published articles cited herein are incorporated herein by reference.

CLAIMS:

1. An expandable or expanded composition comprising either: a) an immiscible blend of polymers comprising one or more polyetherimides, having more than one glass transition temperature wherein the polyetherimide has a glass transition temperature greater than 217° Celsius; b) a miscible blend of polymers, comprising one or more polyetherimides, having a single glass transition temperature greater than 180° Celsius; or, c) a single polyetherimide having a glass transition temperature of greater than 247° Celsius.

2. The expandable or expanded composition according to claim 1 comprising an immiscible blend of polymers having more than one glass transition temperature and one of the polymers has a glass transition temperature greater than 180° Celsius.

3. The expandable or expanded composition according to claim 1 comprising a miscible blend of polymers having a single glass transition temperature greater than 217° Celsius.

4. The expandable or expanded composition according to claim 1 comprising a single virgin polymer having a glass transition temperature of greater than 247° Celsius.

5. The expandable or expanded composition according to claim 1 comprising a blend of a first resin selected from the group consisting of: polysulfones, polyether sulfones, polyphenylene ether sulfones, and mixtures thereof, a second resin comprising a silicone copolymer and a third resin comprising a resorcinol based aryl polyester resin wherein greater than or equal to 50 mole % of the aryl polyester linkages are aryl ester linkages derived from resorcinol.

6. The expandable or expanded composition according to claim 5 wherein the silicone copolymer is selected from the group consisting of; polyimide siloxanes, polyetherimide siloxanes, polyetherimide sulfone siloxanes, polycarbonate siloxanes, polyestercarbonate siloxanes, polysulfone siloxanes, polyether sulfone siloxanes, polyphenylene ether sulfone siloxanes and mixtures thereof.

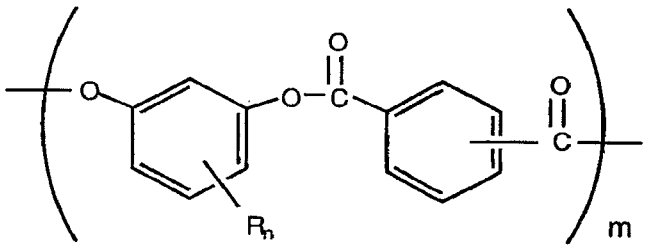
7. The expandable or expanded composition according to claim 6 wherein the silicone copolymer content is from 0.1 to 10.0 wt% of the polymer blend.

8. The expandable or expanded composition according to claim 6 wherein the silicone copolymer has from 20-50 wt% siloxane content.

9. The expandable or expanded composition according to claim 5 wherein the polysulfones, polyether sulfones, polyphenylene ether sulfones and mixtures thereof, have a hydrogen atom to carbon atom ratio of less than or equal to 0.85.

10. The expandable or expanded composition according to claim 5 further comprising one or more metal oxides at 0.1 to 20% by weight of the polymer blend.

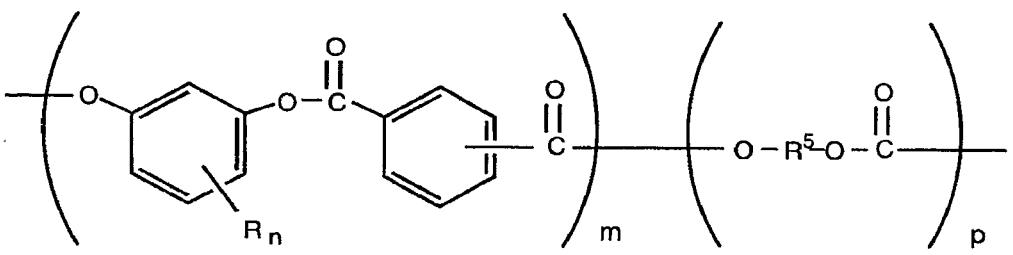
11. The expandable or expanded composition according to claim 5 wherein the resorcinol based aryl polyester has the structure shown below:



wherein R is at least one of C_{1-12} alkyl, C_6-C_{24} aryl, alkyl aryl, alkoxy or halogen; and,

n is 0-4 and m is at least about 8.

12. The expandable or expanded composition according to claim 5 wherein the resorcinol based polyester resin is a copolymer containing carbonate linkages having the structure shown below:



wherein R is at least one of C_{1-12} alkyl, C_6-C_{24} aryl, alkyl aryl, alkoxy or halogen, n is 0-4. R^5 is at least one divalent organic radical, m is about 4 – 150 and p is about 2-200.

13. The expandable or expanded composition according to claim 12 wherein R^5 is derived from a bisphenol compound.

14. An expandable or expanded composition according to claim 1 wherein the immiscible blend of polymers comprises a mixture of: a) a first resin component selected from one or more of the group comprising: polyaryl ether ketones, polyaryl ketones, polyether ketones and polyether ether ketones; with, b) a second resin component comprising at least one polysulfone etherimide having greater than or equal to 50 mole% of the linkages containing at least one aryl sulfone group.

15. An expandable or expanded composition according to claim 14 wherein the polysulfone etherimide contains aryl sulfone and aryl ether linkages such that at least 50 mole % of the repeat units of the polysulfone etherimide contain at least one aryl ether linkage, at least one aryl sulfone linkage and at least two aryl imide linkages.

16. An expandable or expanded composition according to claim 14 wherein at least 50 mole% of the polysulfone etherimide linkages are derived from oxydiphthalic anhydride or a chemical equivalent thereof.

17. An expandable or expanded composition according to claim 14 wherein less than 30 mole% of polysulfone etherimide linkages are derived from a diamine or dianhydride containing an isoalkylidene group.

18. An expandable or expanded composition according to claim 14 wherein the substrate has a heat distortion temperature (HDT) of greater than or equal to 170 °C, measured as per ASTM method D648 at 66 psi (0.46 Mpa) on a 3.2 mm sample.

19. An expandable or expanded composition according to claim 14 wherein the polysulfone etherimide is present from 30-70 wt% of the substrate.

20. An expandable or expanded composition according to claim 14 wherein the polysulfone etherimide is essentially free of benzylic protons.

21. An expandable or expanded composition according to claim 14 wherein the one or more polyaryl ether ketone, polyaryl ketone, polyether ketone, and polyether ether ketone have a crystalline melting point from 300° to 380 °C.

22. An expandable or expanded composition according to claim 14 wherein the polysulfone etherimide has a glass transition temperature (Tg), from 250° to 350 °C.

23. An expandable or expanded composition according to claim 14 wherein the polymer blend has at least two different glass transition temperatures, as measured by ASTM method D5418, wherein the first glass transition temperature is from 120°-200 °C and the second glass transition temperature is from 250° – 350 °C.

24. An expandable or expanded composition having improved flame retardance according to claim 1 comprising a blend of a first resin selected from the group consisting of: polyimides, polyetherimides, polyetherimide sulfones, and mixtures thereof, a second resin comprising a silicone copolymer and a third resin comprising a resorcinol based aryl polyester resin wherein greater than or equal to 50 mole % of the aryl polyester linkages are aryl ester linkages derived from resorcinol.

25. An expandable or expanded composition according to claim 24 wherein the silicone copolymer is one or more selected from the group consisting of: polyimide siloxanes, polyetherimide siloxanes, polyetherimide sulfone siloxanes, polycarbonate siloxanes, polyestercarbonate siloxanes, polysulfone siloxanes, polyether sulfone siloxanes, and polyphenylene ether sulfone siloxanes.

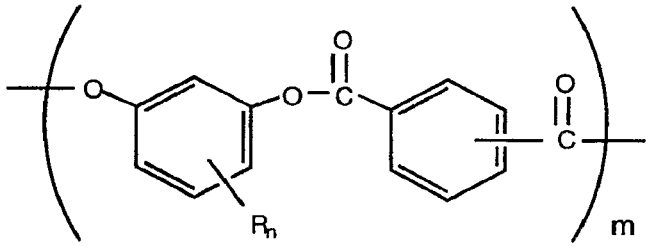
26. An expandable or expanded composition according to claim 24 wherein the silicone copolymer content is from 0.1 to 10.0 wt% of the polymer blend.

27. An expandable or expanded composition according to claim 24 wherein the silicone copolymer has from 20-50 wt% siloxane content.

28. An expandable or expanded composition according to claim 24 wherein the polyimides, polyetherimides, polyetherimide sulfones and mixtures thereof, have a hydrogen atom to carbon atom ratio of less than or equal to 0.75.

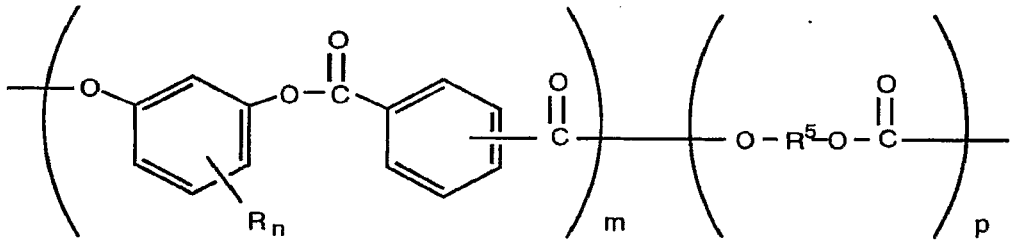
29. An expandable or expanded composition according to claim 24 further comprising one or more metal oxides at 0.1 to 20% by weight of the polymer blend.

30. An expandable or expanded composition according to claim 24 wherein the resorcinol based aryl polyester has the structure shown below:



wherein R is at least one of C_{1-12} alkyl, C_6-C_{24} aryl, alkyl aryl, alkoxy or halogen, n is 0-4 and m is at least about 8.

31. An expandable or expanded composition according to claim 24 wherein the resorcinol based polyester resin is a copolymer containing carbonate linkages having the structure shown below:



wherein R is at least one of C_{1-12} alkyl, C_6-C_{24} aryl, alkyl aryl, alkoxy or halogen, n is 0-4. R^5 is at least one divalent organic radical, m is about 4 – 150 and p is about 2-200.

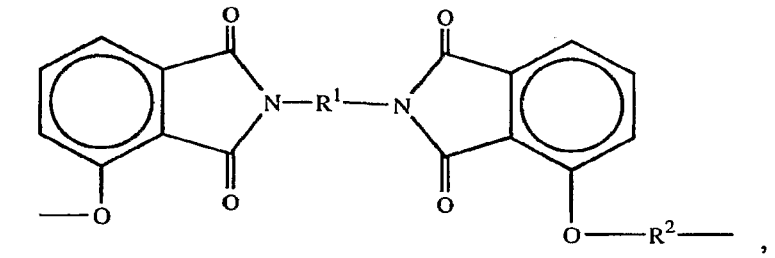
32. An expandable or expanded composition according to claim 31 wherein R^5 is derived from a bisphenol compound.

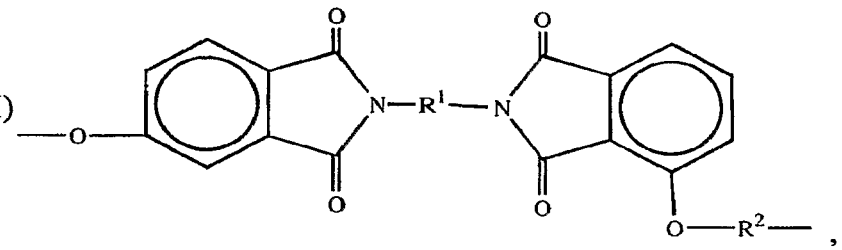
33. An expandable or expanded composition according to claim 24 wherein the polyimide, polyetherimide, or polyetherimide sulfone is made from

aryl dianhydrides selected from the group consisting of: bisphenol A dianhydride, oxydiphthalic anhydride, pyromellitic dianhydride, diphthalic anhydride, sulfonyl dianhydride, sulfur dianhydride, benzophenone dianhydride and mixtures thereof; and,

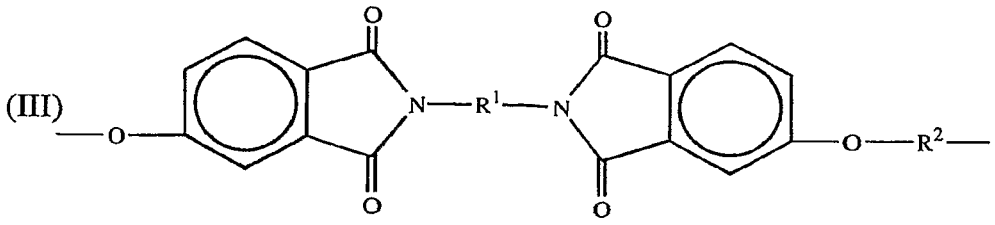
aryl diamines selected from the group consisting of: meta phenylene diamine, para phenylene diamine, diamino diphenyl sulfone, oxydianiline, bis amino phenoxy benzene, bis aminophenoxy biphenyl, bis aminophenyl phenyl sulfone, diamino diphenyl sulfide and mixtures thereof.

34. An expandable or expanded composition according to claim 1 comprising a copolyetherimide having a glass transition temperature of at least about 218°C, said copolyetherimide comprising structural units of the formulas (I) and (II):

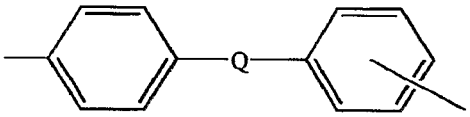
(I) 

(II) 

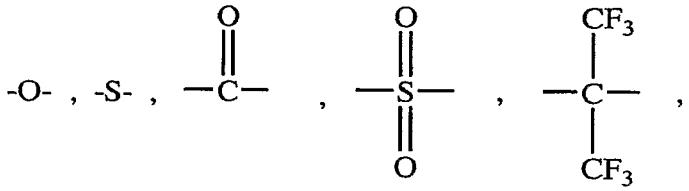
and optionally structural units of the formula (III):

(III) 

wherein R^1 comprises an unsubstituted C_{6-22} divalent aromatic hydrocarbon or a substituted C_{6-22} divalent aromatic hydrocarbon comprising halogen or alkyl substituents or mixtures of said substituents; or a divalent radical of the general formula (IV):

(IV) 

group wherein the unassigned positional isomer about the aromatic ring is either meta or para to Q, and Q is a covalent bond or a member selected from the consisting of formulas (V):

(V) 

and an alkylene or alkylidene group of the formula C_yH_{2y}, wherein y is an integer from 1 to 5 inclusive, and R^2 is a divalent aromatic radical; the weight ratio of units of formula (I) to those of formula (II) being in the range of about 99.9:0.1 and about 25:75.

35. An expandable or expanded composition according to claim 34 comprising a copolyetherimide having a Tg greater than 225°C.

36. An expandable or expanded composition according to claim 34 comprising a copolyetherimide comprising structural units of the formula (III).

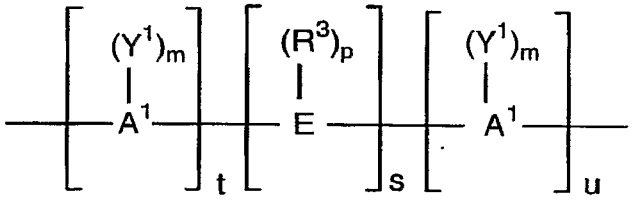
37. An expandable or expanded composition according to claim 34 wherein R^1 is derived from at least one diamine selected from the group consisting of meta-phenylenediamine; para-phenylenediamine; 2-methyl-4,6-diethyl-1,3-phenylenediamine; 5-methyl-4,6-diethyl-1,3-phenylenediamine; bis(4-aminophenyl)-2,2-propane; bis(2-chloro-4-amino-3,5-diethylphenyl)methane, 4,4'-diaminodiphenyl, 3,4'-diaminodiphenyl, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 4,4'-diaminodiphenyl sulfone, 3,4'-diaminodiphenyl sulfone, 4,4'-diaminodiphenyl ketone, 3,4'-diaminodiphenyl ketone, 2,4-toluenediamine; and mixtures thereof.

38. An expandable or expanded composition according to claim 34 wherein R^2 is derived from at least one dihydroxy-substituted aromatic hydrocarbon of the formula (VI):

HO---D---OH

wherein D has the structure of formula (VII):

(VII)



wherein A^1 represents an aromatic group;

E comprises a sulfur-containing linkage, sulfide, sulfoxide, sulfone; a phosphorus-containing linkage, phosphinyl, phosphonyl; an ether linkage; a carbonyl group; a tertiary nitrogen group; a silicon-containing linkage; silane; siloxy; a cycloaliphatic group; cyclopentylidene, 3,3,5-trimethylcyclopentylidene, cyclohexylidene, 3,3-dimethylcyclohexylidene, 3,3,5-trimethylcyclohexylidene, methylcyclohexylidene, 2-[2.2.1]-bicycloheptylidene, neopentylidene, cyclopentadecylidene, cyclododecylidene, adamantylidene; an alkylene or alkylidene group, which group may optionally be part of one or more fused rings attached to one or more aromatic groups bearing one hydroxy substituent; an unsaturated alkylidene group; or two or

more alkylene or alkylidene groups connected by a moiety different from alkylene or alkylidene and selected from the group consisting of an aromatic linkage, a tertiary nitrogen linkage; an ether linkage; a carbonyl linkage; a silicon-containing linkage, silane, siloxy; a sulfur-containing linkage, sulfide, sulfoxide, sulfone; a phosphorus-containing linkage, phosphinyl, and phosphonyl;

R^3 comprises hydrogen; a monovalent hydrocarbon group, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, or cycloalkyl;

Y^1 independently at each occurrence is selected from the group consisting of an inorganic atom, a halogen; an inorganic group, a nitro group; an organic group, a monovalent hydrocarbon group, alkenyl, allyl, alkyl, aryl, aralkyl, alkaryl, cycloalkyl, and an alkoxy group;

the letter "m" represents any integer from and including zero through the number of positions on A^1 available for substitution;

the letter "p" represents an integer from and including zero through the number of positions on E available for substitution;

the letter "t" represents an integer equal to at least one;

the letter "s" represents an integer equal to either zero or one; and,

"u" represents any integer including zero.

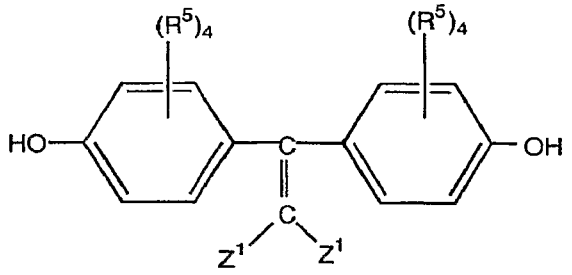
39. An expandable or expanded composition according to claim 34 wherein R^2 structural units in each of formulas (I), (II) and (III) are the same.

40. An expandable or expanded composition according to claim 34 wherein at least a portion of R^2 structural units in at least two of formulas (I), (II) and (III) are not the same.

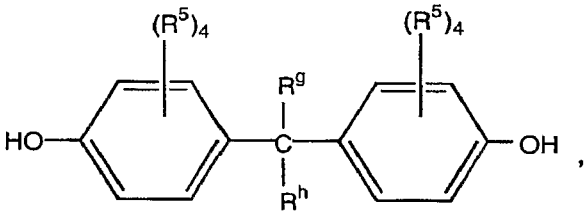
41. An expandable or expanded composition according to claim 34 wherein R^2 is derived from at least one dihydroxy-substituted aromatic hydrocarbon selected from the group consisting of 4,4'-(cyclopentylidene)diphenol; 4,4'-(3,3,5-

trimethylcyclopentylidene)diphenol; 4,4'-(cyclohexylidene)diphenol; 4,4'-(3,3-dimethylcyclohexylidene)diphenol; 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol; 4,4'-(methylcyclohexylidene)diphenol; 4,4'-bis(3,5-dimethyl)diphenol, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane; 4,4-bis(4-hydroxyphenyl)heptane; 2,4´-dihydroxydiphenylmethane; bis(2-hydroxyphenyl)methane; bis(4-hydroxyphenyl)methane; bis(4-hydroxy-5-nitrophenyl)methane; bis(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 1,2-bis(4-hydroxyphenyl)ethane; 1,1-bis(4-hydroxy-2-chlorophenyl)ethane; 2,2-bis(4-hydroxyphenyl)propane; 2,2-bis(3-phenyl-4-hydroxyphenyl)propane; 2,2-bis(4-hydroxy-3-methylphenyl)propane; 2,2-bis(4-hydroxy-3-ethylphenyl)propane; 2,2-bis(4-hydroxy-3-isopropylphenyl)propane; 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane; 3,5,3',5'-tetrachloro-4,4'-dihydroxyphenyl)propane; bis(4-hydroxyphenyl)cyclohexylmethane; 2,2-bis(4-hydroxyphenyl)-1-phenylpropane; 2,4'-dihydroxyphenyl sulfone; dihydroxy naphthalene, 2,6-dihydroxy naphthalene; hydroquinone; resorcinol; C_{1-3} alkyl-substituted resorcinols; 2,2-bis-(4-hydroxyphenyl)butane; 2,2-bis-(4-hydroxyphenyl)-2-methylbutane; 1,1-bis-(4-hydroxyphenyl)cyclohexane; bis-(4-hydroxyphenyl); bis-(4-hydroxyphenyl)sulphide; 2-(3-methyl-4-hydroxyphenyl-2-(4-hydroxyphenyl)propane; 2-(3,5-dimethyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane; 2-(3-methyl-4-hydroxyphenyl)-2-(3,5-dimethyl-4-hydroxyphenyl)propane; bis-(3,5-dimethylphenyl-4-hydroxyphenyl)methane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)ethane; 2,2-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)propane; 2,4-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)-2-methylbutane; 3,3-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)pentane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)cyclopentane; 1,1-bis-(3,5-dimethylphenyl-4-hydroxyphenyl)cyclohexane; bis-(3,5-dimethylphenyl-4-hydroxyphenyl)sulphide, 3-(4-hydroxyphenyl)-1,1,3-trimethylindan-5-ol, 1-(4-hydroxyphenyl)-1,3,3-trimethylindan-5-ol, and 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indene]-6,6'-diol.

42. An expandable or expanded composition according to claim 34 wherein R^2 is derived from at least one dihydroxy-substituted aromatic hydrocarbon selected from the group consisting of those of the formula (IX):

(IX) 

where independently each R^5 is hydrogen, chlorine, bromine or a C_{1-30} monovalent hydrocarbon or hydrocarbonoxy group, each Z^1 is hydrogen, chlorine or bromine, subject to the provision that at least one Z^1 is chlorine or bromine; and those of the formula (X):

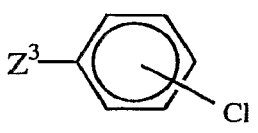
(X) 

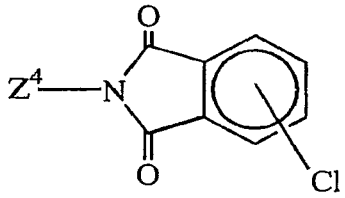
where independently each R^5 is as defined hereinbefore, and independently R^g and R^h are hydrogen or a C_{1-30} hydrocarbon group.

43. An expandable or expanded composition according to claim 42 wherein R^2 is derived from bisphenol A.

44. An expandable or expanded composition according to claim 34 further comprising structural units derived from at least one chain termination agent.

45. An expandable or expanded composition according to claim 44 wherein the chain termination agent is at least one unsubstituted or substituted member selected from the group consisting of alkyl halides, alkyl chlorides, aryl halides, aryl chlorides, and chlorides of formulas (XVII) and (XVIII):

(XVII) 

(XVIII) 

wherein the chlorine substituent is in the 3- or 4-position, and Z^3 and Z^4 comprise a substituted or unsubstituted alkyl or aryl group.

46. An expandable or expanded composition according to claim 45 wherein the chain termination agent is at least one member selected from the group consisting of monochlorobenzophenone, monochlorodiphenylsulfone; a monochlorophthalimide; 4-chloro-N-methylphthalimide, 4-chloro-N-butylphthalimide, 4-chloro-N-octadecylphthalimide, 3-chloro-N-methylphthalimide, 3-chloro-N-butylphthalimide, 3-chloro-N-octadecylphthalimide, 4-chloro-N-phenylphthalimide, 3-chloro-N-phenylphthalimide; a mono-substituted bis-phthalimide; a monochlorobisphthalimidobenzene; 1-[N-(4-chlorophthalimido)]-3-(N-phthalimido)benzene; 1-[N-(3-chlorophthalimido)]-3-(N-phthalimido)benzene; monochlorobisphthalimidodiphenyl sulfone, monochlorobisphthalimidodiphenyl ketone, a monochlorobisphthalimidophenyl ether; 4-[N-(4-chlorophthalimido)]phenyl-4'-(N-phthalimido)phenyl ether; 4-[N-(3-chlorophthalimido)phenyl]-4'-(N-phthalimido)phenyl ether, and the corresponding isomers of the latter two compounds derived from 3,4'-diaminodiphenyl ether.

47. An expandable or expanded composition according to claim 34 wherein the weight ratio of units of formula I to those of formula II is in the range of between about 99:1 and about 25:75.

48. An expandable or expanded composition according to claim 34 wherein the expandable or expanded composition has a heat distortion temperature at 0.455 MPa of at least 205°C.

49. An expandable or expanded composition according to claim 34 wherein the expandable or expanded composition has a heat distortion temperature at 0.455 MPa of at least 210°C.

50. An expandable or expanded composition according to claim 34 wherein the expandable or expanded composition has a temperature of transition between the brittle and ductile states of at most 30°C as measured by ASTM method D3763.

51. The expandable or expanded composition according to claim 1 further comprising a reinforcing filler.

52. The expandable or expanded composition according to claim 1 further comprising an electrically conductive additive.

53. The expandable or expanded composition according to claim 1 wherein the expandable or expanded composition comprises multiple layers.

54. The expanded composition according to claim 1 wherein the expanded composition has a bulk density of 3 to 25 kilograms per cubic meter.

55. The expanded material according to claim 54 wherein the expanded material is flexible.

56. The expanded material according to claim 55 wherein the expanded material is rigid.

57. The expandable or expanded material of Claim 1 further comprising one or more fillers.

58. An article comprising the expanded material of Claim 1 laminated to one or more films or sheets.

59. The article according to claim 58 wherein the film or sheet comprises either: a) an immiscible blend of polymers having more than one glass transition temperature and one of the polymers has a glass transition temperature greater than 180 degrees Celsius; b) a miscible blend of polymers having a single glass transition temperature greater than 217 degrees Celsius; or, c) a single virgin polymer having a glass transition temperature of greater than 247 degrees Celsius.

60. An article comprising two or more portions of the expanded material of Claim 1 adhered together.