(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 July 2007 (05.07.2007)

PCT

(10) International Publication Number
WO 2007/075365 A2

(51) International Patent Classification:
C08L 79/08 (2006.01)

(21) International Application Number:
PCT/US2006/047800

(22) International Filing Date:
14 December 2006 (14.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

11/314,542	21 December 2005 (21.12.2005)	US
11/383,639	16 May 2006 (16.05.2006)	US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier applications:

US	11/228,728 (CON)
Filed on	16 September 2005 (16.09.2005)
US	11/228,729 (CON)
Filed on	16 September 2005 (16.09.2005)
US	11/229,455 (CON)
Filed on	16 September 2005 (16.09.2005)

(71) Applicant *(for all designated States except US)*: **GENERAL ELECTRIC COMPANY** [US/US]; 1 River Road, Schenectady, NY 12345 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ODLE, Roy, Ray** [US/US]; 7401 Saverkraut Lane North, Mt. Vernon, IN 47620 (US). **SHETH, Kapil, Chandrakant** [IN/US]; 331 Hope Court, Evansville, IN 47712 (US). **DONAVAN, Michael, Stephen** [US/US]; 706 Sunflower Cr., Evansville, IN 47712 (US). **SANNER, Mark, A.** [US/US]; 6166 Laurel Ridge Drive, Newburgh, IN 47630 (US). **SINGH, Rajendra, Kashinath** [IN/US]; 8500 Aster Lane, Evansville, IN 47712 (US). **GALLUCCI, Robert, Russell** [US/US]; 1109 Tanglewood Drive, Mt. Vernon, IN 47620 (US).

(74) Agents: **TOOP, Barbara, A.** et al.; GENERAL ELECTRIC COMPANY, Global Patent Operation, 187 Danbury Road, Suite 204, Wilton, CT 06897 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US (patent), UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** ANNULAR OR TUBULAR SHAPED ARTICLES OF NOVEL POLYMER BLENDS

(57) **Abstract:** The present invention is directed to a tubular article of manufacture in an annular or tubular shape having an outer diameter, an inner diameter and a length comprising one or more materials selected from the group consisting of: 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.

WO 2007/075365 A2

ANNULAR OR TUBULAR SHAPED ARTICLES OF NOVEL POLYMER BLENDS

RELATED APPLICATIONS

The present application is a continuation-in-part of each of the following United States patent applications: USSN 11/228,728, filed September 16, 2005, in the name of Gallucci et al., titled "Flame Retardant Polysulfone Blends"; USSN 11/228,729, filed September 16, 2005, in the name of Gallucci et al., titled Flame Retardant Polymer Blends"; and, USSN 11/229,455, filed September 16, 2005, in the name of Gallucci et al., titled "Improved Polyaryl Ether Ketone Polymer Blends" and USSN 11/314,542, filed December 21, 2005, in the name of Gallucci et al., titled "Annular or Tubular Shaped Articles of Novel Polymer Blends".

FIELD OF THE INVENTION

The present invention is directed to tubular or annular shaped articles of manufacture comprising at least one polyetherimide polymer having a Tg above about 180 degrees Celsius having a length, an inner diameter and an outer diameter.

BACKGROUND

In a variety of end-use applications requiring the use of annular shaped articles of manufacture, there is a need for materials which have good chemical resistance as well as high temperature properties allowing for prolonged use in high temperature environments.

With the current and sustained rise in oil prices, there is a need for metal replacement parts in vehicles that are capable of reducing the overall weight of the a vehicle while still providing the long term use characteristics of metal. Under the hood fluid and gas transfer means added weight and reduced gas mileage to vehicles, causing unnecessary expense to the vehicles owner. Radiator and coolant parts as well as tubes and conduits made of metal could be replaced with lighter plastic parts, leading to reduced manufacturing costs and increased fuel efficiency. Such plastic parts

would need to be capable of withstanding prolonged temperatures above the boiling point of water, and have chemical resistance to common automotive coolants.

In the oil exploration and oil supply area there is a need for pipe and pipe shaped articles capable of performing at elevated temperatures and exposed to a wide variety of organic materials. During oil pumping operations, it is common to insert hot water and/or steam into an oil well, to displace oil to the surface of the well. In these conditions there is a need for pipe or wire coating having good high temperature properties as well as chemical resistance to the wide range of organic compounds found in oil.

There is a continuing need in the field of high heat polymers for materials which are capable of use in high temperature environments and applications. In particular, there is a high demand for improved pipe and annular shaped articles of manufacture in a variety of technologies.

BRIEF DESCRIPTION

The present invention is directed to tubular articles of manufacture in an annular or tubular shape having an outer diameter, an inner diameter and a length comprising one or more materials selected from the group consisting of: 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 present invention is also directed to tubular articles of manufacture as detailed above wherein the polyetherimide has a hydrogen atom to carbon atom ratio of between about 0.4 and 0.85 and/or is essentially free of benzylic protons.

The present invention is still yet further directed to a tubular article of manufacture as described above wherein the outer diameter of the article is substantially the same throughout the length.

DETAILED DESCRIPTPION

For purposes of the present invention, the terms "pipe", "tubing" and "hose" mean tubular or annular members of definite or indefinite length which may be made of different materials and may include wall structure of tubular members (ie round square octagonal, etc.) and/or an end structure of tubular members of definite length.

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 present invention is directed to tubular articles of manufacture in an annular or tubular shape having an outer diameter, an inner diameter and a length comprising one or more materials selected from the group consisting of: 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 tube shaped articles may further comprise a polyetherimide has a hydrogen atom to carbon atom ratio of between about 0.4 and about 0.85. The hydrogen atom number to carbon atom number may also be from about 0.50 to about 0.80 or from about 0.55 to about 0.75, or from about 0.60 to about 0.70.

The tube shaped articles may also comprise a polyetherimide that is essentially free of benzylic protons.

In terms of physical dimensions the annular article according to the present invention may have an outer diameter, an inner diameter and a length. The annular article may have a constant, or approximately constant outer diameter and a constant or approximately constant inner diameter. Alternatively, the outer diameter and/or the inner diameter may both or individually change over the length of the annular article. The annular article may have a thickness, defined as the outer diameter minus the inner diameter, which is less than, greater than or equal to the inner radius.

The tubular article of manufacture according to the present invention may also be a coating on a shaped article having a different composition than the coating. For example, the article may take the form of a coating on a solid metal wire, or as a coating on a solid cable core. In an alternate embodiment the annular article may be completely hollow or cover the exterior surface of a hollow article.

Materials:

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.

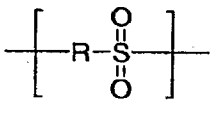
Disclosed herein are electrical connectors comprising a polymers blend, wherein some or all of one surface of the polymer blend is coated with a covering, wherein the covering material is of a different composition than the polymer blend, and, wherein the polymer blend comprises: a) a first resin selected 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.

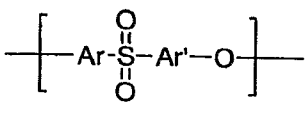
Polysulfones comprise repeating units having the structure of Formula I:



(I)

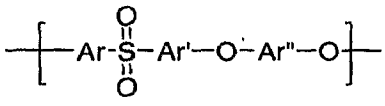
wherein R is an aromatic group comprising carbon-carbon single bonds, carbon-oxygen-carbon bonds or carbon-carbon and carbon-oxygen-carbon single bonds and the single bonds form a portion of the polymer backbone.

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.

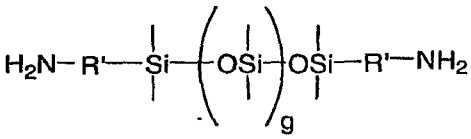
2. The Silicone Component Of The Blend

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.

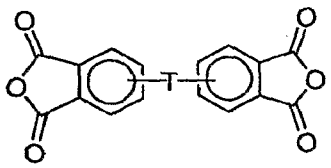
Siloxane polyetherimide copolymers are a specific embodiment of the siloxane copolymer that may be used in the polymer blend. Examples of such siloxane polyetherimide copolymers are shown in US Patents No. 4,404,350, 4,808,686 and

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.



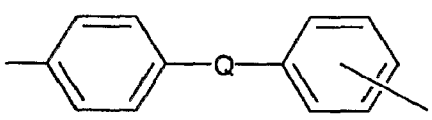
Formula IV

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



Formula (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



Formula (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

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

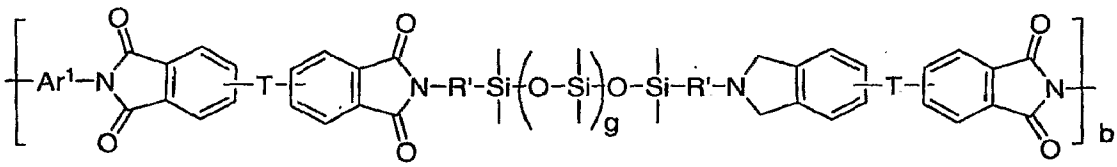
4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl sulfone dianhydride,

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.



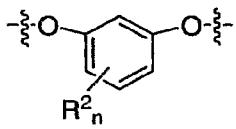
Formula VIII

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.



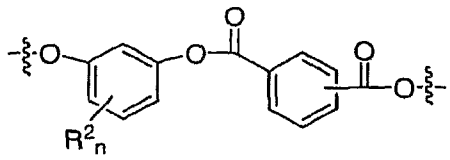
Formula IX

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.

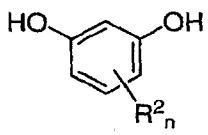
Suitable dicarboxylic acids include monocyclic and polycyclic aromatic dicarboxylic acids. Exemplary monocyclic dicarboxylic acids include isophthalic acid, terephthalic acid, or mixtures of isophthalic and terephthalic acids. Polycyclic dicarboxylic acids include diphenyl dicarboxylic acid, diphenylether 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

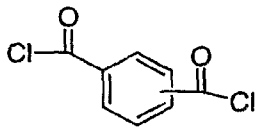
Polymers comprising resorcinol arylate polyester units may be made by an interfacial polymerization method. To prepare polymers comprising resorcinol arylate polyester units substantially free of anhydride linkages a method can be employed wherein the first step combines a resorcinol group and a catalyst 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.

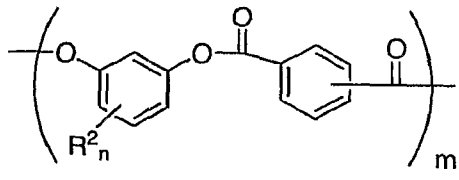
Suitable mono-carboxylic acid chlorides include monocyclic, mono-carboxylic acid chlorides, such as benzoyl chloride, C_1-C_{22} alkyl-substituted benzoyl chloride, toluoyl chloride, halogen-substituted benzoyl chloride, bromobenzoyl chloride, cinnamoyl chloride, 4-nadimidobenzoyl chloride, and mixtures 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.

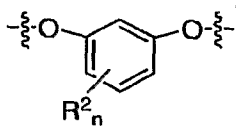
In one of its embodiments articles of manufacture comprise thermally stable resorcinol arylate polyesters made by the described method and substantially free of anhydride linkages linking at least two mers of the polyester chain. In a particular embodiment said polyesters comprise dicarboxylic acid residues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



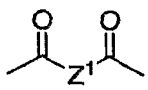
Formula XIII

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.

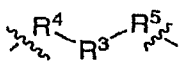
Also included are articles comprising a resorcinol arylate copolyesters containing soft-block segments as disclosed in commonly owned U.S. Patent No. 5,916,997. The term soft-block as used herein, indicates that some segments of the polymers are made from non-aromatic monomer units. Such non-aromatic 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.

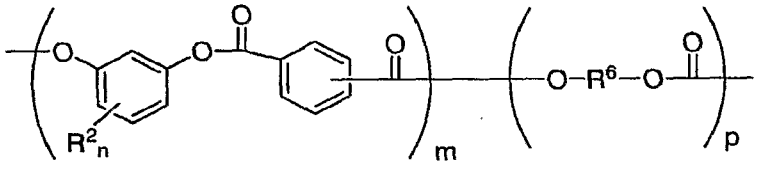
In another of its embodiments the resorcinol based polyarylate can be a block copolyestercarbonate comprising resorcinol arylate-containing block segments in combination with organic carbonate block segments. The segments comprising resorcinol arylate chain members in such copolymers are substantially 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

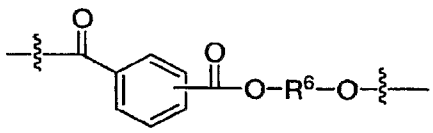
phenylene radicals are preferred. Both A^1 and A^2 are often p-phenylene, although both may be o- or m-phenylene or one o- or m-phenylene and the other p-phenylene.

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

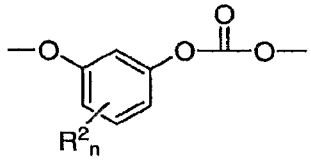
(a) an ester linkage between a suitable dicarboxylic acid residue of an arylate group and an —O—R^6—O— group of an organic carbonate group, for example as typically illustrated in Formula XVIII, wherein R^6 is as previously defined :



Formula XVIII

and

(b) 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,

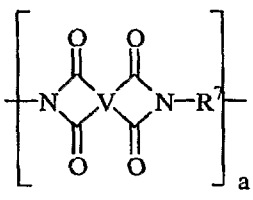
about 0.1 to about 10% by weight of silicone copolymer

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

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

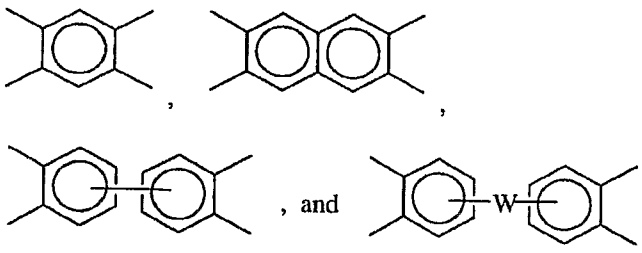
is contemplated.

Polyimides have the general formula (XX)



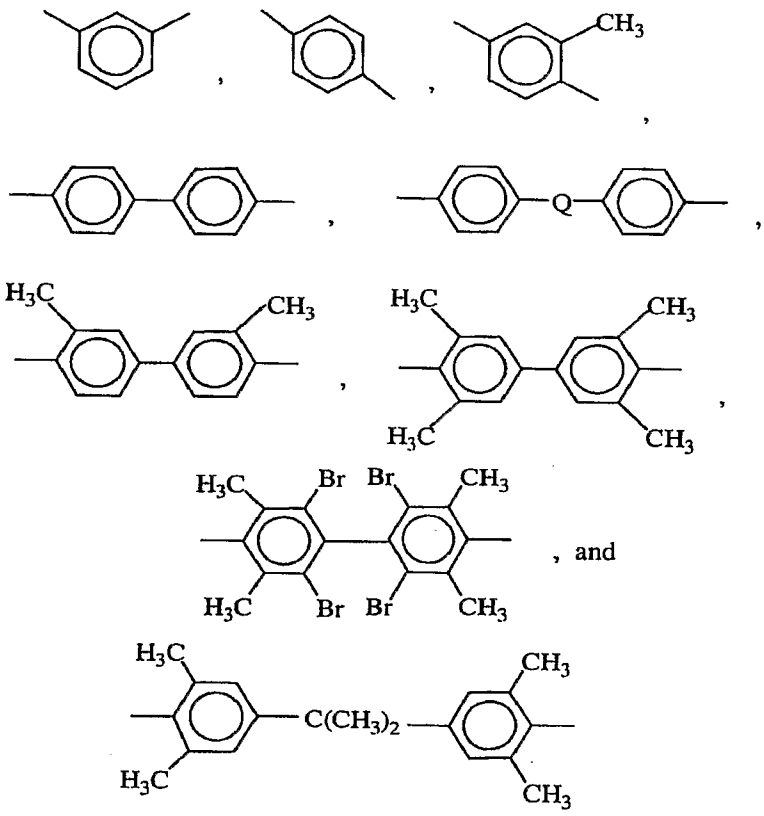
(Formula XX)

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)

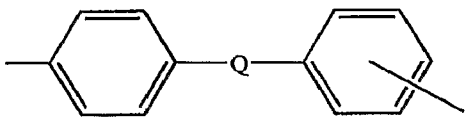
wherein W is a divalent group selected from the group consisting of -O-, -S-, -C(O)-, SO_2-, -SO-, $-C_yH_{2y}-$ (y being an integer having a value of 1 to about 8), and fluoronated derivatives thereof, including perfluoroalkylene groups, or a group of the formula -O-Z-O- wherein the divalent bonds of 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)

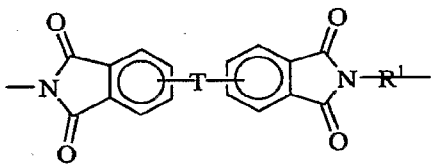


(Formula VI)

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.

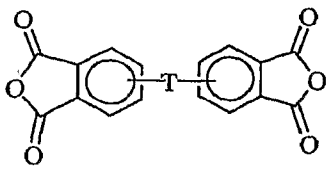
Polyetherimide resins may comprise more than 1, typically about 10 to about 1000 or more, or, more specifically, about 10 to about 500 structural units, of the formula (XXIII)



(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;

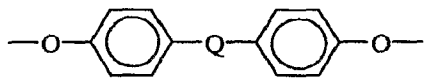
4-(2,3-dicarboxyphenoxy)-4'-(3,4-dicarboxyphenoxy)diphenyl-2,2-propane dianhydride;

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)



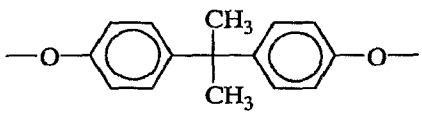
(Formula XXIV)

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)



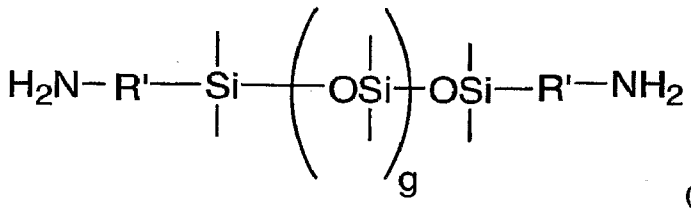
(Formula XXV)

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.

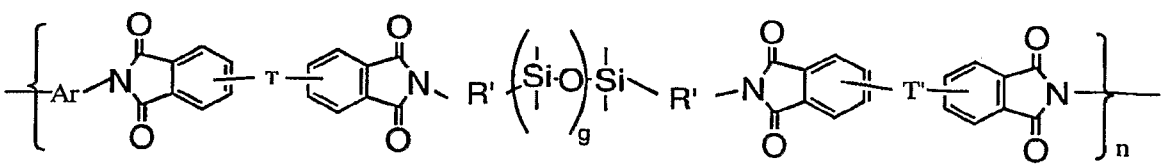
Siloxane polyetherimide copolymers are a specific embodiment of the siloxane copolymer that may be used. Examples of such siloxane polyetherimides are shown in US Patents 4,404,350, 4,808,686 and 4,690,997. In one instance polyetherimide siloxanes can be prepared in a manner similar to that used for 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.

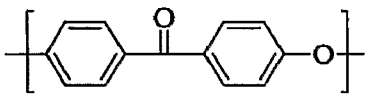
In still other instances load bearing capability of the phase separated polymer blend will be shown by a flexural modulus of greater than or equal to about 200 megapascals (MPa) as measured on a 3.2 mm bar, for example as measured by ASTM method D5418, at 200 °C.

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.

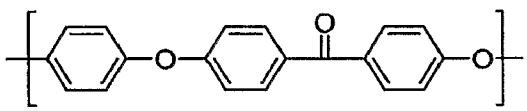
As used herein the term polyaryl ether ketones (PAEK) comprises several polymer types containing aromatic rings, usually phenyl rings, linked primarily by ketone and ether groups in different sequences. Examples of PAEK resins include polyether

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

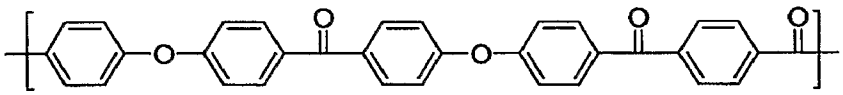
For example, several polyaryl ether ketones which are highly crystalline, with melting points above 300 °C, can be used in the phase separated blends. Examples of these crystalline polyaryl ether ketones are shown in the structures XXVI, XXVII, XXVIII, XXIX, and XXX.



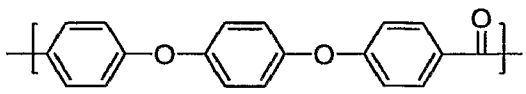
Formula XXVI



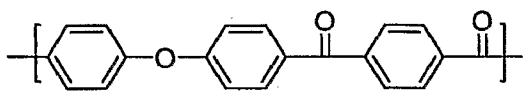
Formula XXVII



Formula XXVIII

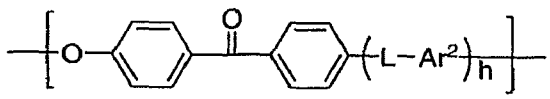


Formula XXIX



Formula 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):



Formula 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.

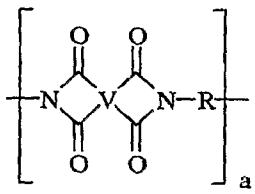
The process is described in, for example, US Patent 4,176,222. The process comprises heating in the temperature range of 100 to 400 °C, (i) a substantially equimolar mixture of: (a) a bisphenol; and, (b.i) a dihalobenzenoid compound, and/or (b.ii) a halophenol, in which in the dihalobenzenoid compound 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.

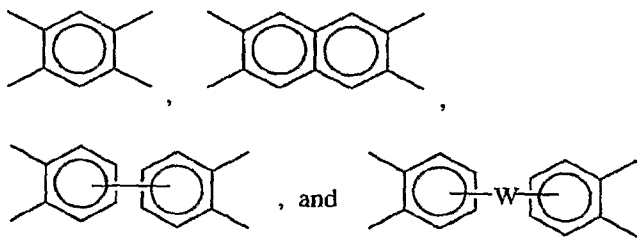
The polyaryl ether ketones may have a reduced viscosity of greater than or equal to about 0.4 to about 5.0 dl/g, as measured in concentrated sulfuric acid at 25 °C. PAEK weight average molecular weight (Mw) may be about 5,000 to about 150,000 g/mole. In other instances Mw may be about 10,000 to about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



Formula (VII)

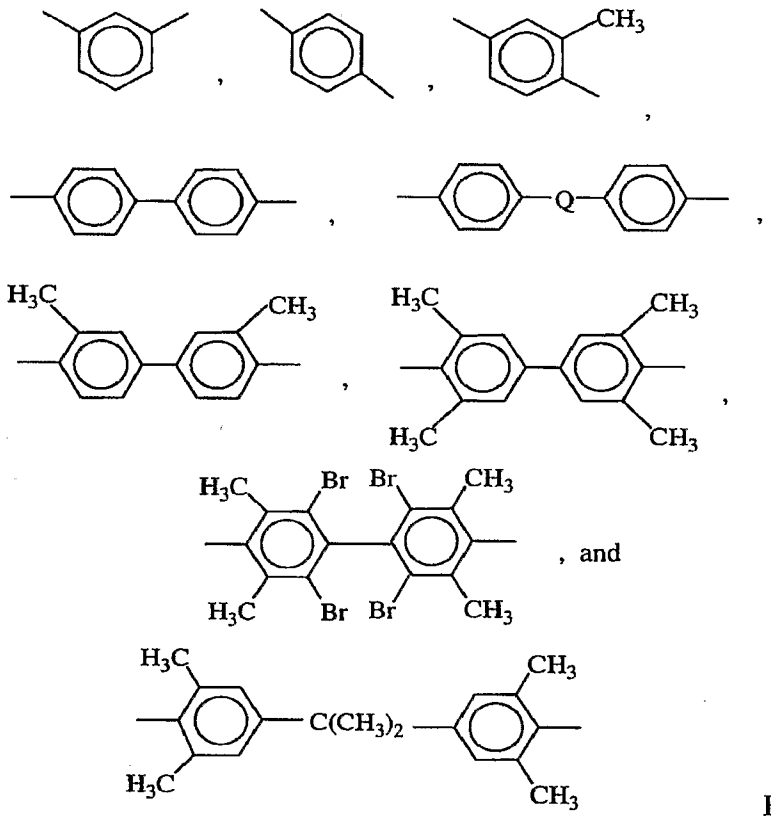
wherein a is more than 1, typically about 10 to about 1000 or more, or, more specifically, about 10 to about 500; and V is a tetravalent linker without limitation, as long as the linker does not impede synthesis or use of the polysulfone etherimide. Suitable linkers include but are not limited to: (a) 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,



Formula (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.



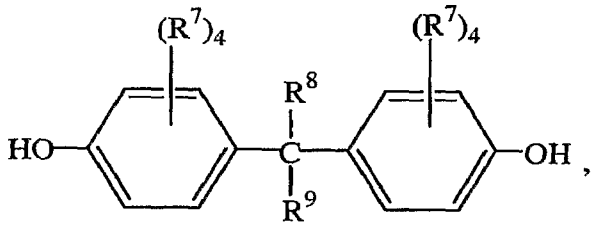
Formula (IX)

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):



Formula (X);

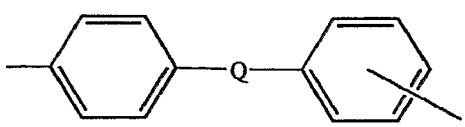
where each R^7 is independently hydrogen, chlorine, bromine, alkoxy, aryloxy or a C_{1-30} monovalent hydrocarbon or hydrocarbonoxy group, and R^8 and R^9 are independently hydrogen, aryl, alkyl fluoro groups or C_{1-30} hydrocarbon groups.

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;

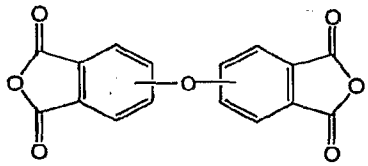
1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride; and,

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.

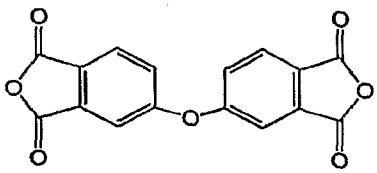
The term "oxydiphthalic anhydride" means the oxydiphthalic anhydride of the formula (XII)



Formula (XII)

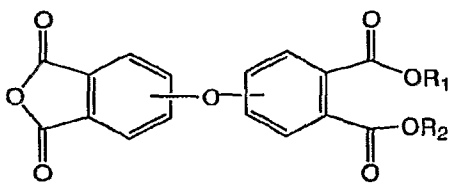
and derivatives thereof as further defined below.

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)



Formula (XIII)

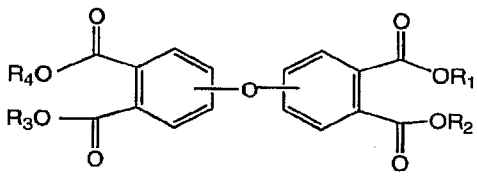
As mentioned above, derivatives of oxydiphthalic anhydrides may be employed to make polysulfone etherimides. Examples of a derivatized anhydride group which can function as a chemical equivalent for the oxydiphthalic anhydride in imide forming reactions, includes oxydiphthalic anhydride derivatives of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



Formula (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)



Formula (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.

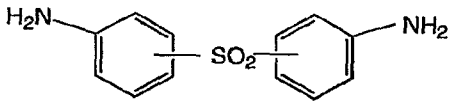
Copolymers of polysulfone etherimides which include structural units derived from imidization reactions of mixtures of the oxydiphthalic anhydrides listed above having two, three, or more different dianhydrides, and a more or less equal molar amount of an organic diamine with a flexible linkage, are 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)

$$H_2N—Ar—SO_2—Ar—NH_2$$ Formula (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)



Formula (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.

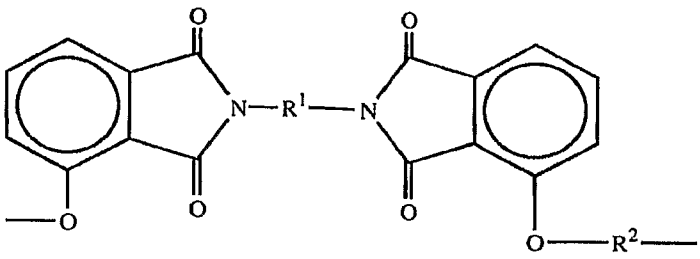
In some instances the composition will have at least two distinct glass transition temperatures (Tg), a first Tg from the PAEK resin, or a partially miscible PAEK blend, and a second Tg associated with the polysulfone etherimide resin, or mixture where such resin predominates. These glass transition 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.

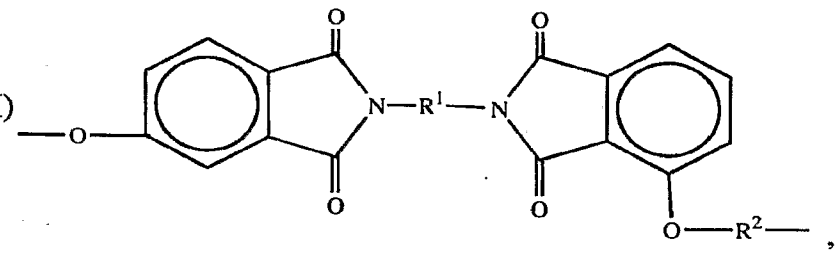
In another embodiment the polysulfone etherimide PEAK blends will have melt viscosity of about 200 Pascal-seconds to about 10,000 Pascal-seconds (Pa-s) at 380°C as measured by ASTM method D3835 using a capillary rheometer with a shear rate of 100 to 10000 1/sec. Resin blends having a melt viscosity of 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.

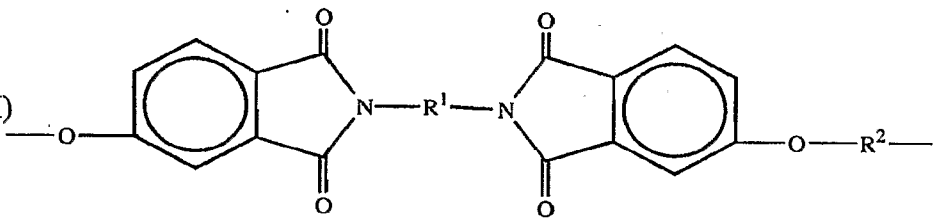
D. Co-Polyetherimides

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):

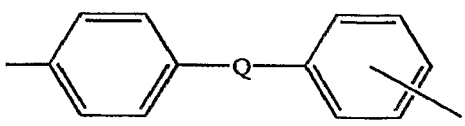
(I) 

(II) 

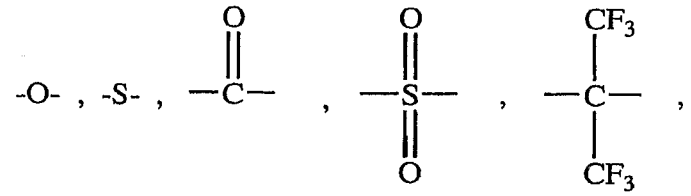
and optionally structural units of the formula (III):

(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.

D1. Blends

The present invention is also directed to A tubular article of manufacture in an annular or tubular shape having an outer diameter, an inner diameter and a length comprising one or more materials selected from the group consisting of: 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 blended with, one or more, of the following polymers: tetrafluoroethylene homopolymers, its copolymers, and terpolymers with hexafluoropropylene, vinylidene fluoride, perfluorovinylethers, vinyl fluoride, ethylene, amorphous thermoplastic polymers including PPSU (polyphenylene sulfone), PI (polyimide), PEI (poly(ether imide)), PSU (polysulfone), PC (Polycarbonate), PPO (polyphenylene ether), PMMA (poly methyl methacrylate), ABS, (acrylonitrile butadiene styrene), PS (polystyrene) and, PVC (polyvinylchloride), Crystalline thermoplastic resins including PFA (per fluoro aalkoxy alkane), MFA (co-polymer of TFE tetra fluoro ethylene and PFVE perfluorinated vinyl ether), FEP (Fluorinated ethylene propylene polymers), PPS

(poly(phenylene sulfide), PEK (poly(ether ketone), PEEK (poly(ether-ether ketone), ECTFE (ethylene chloro trifluoro ethylene) , PVDF(polyvinylidene fluoride), PTFE (polytetrafluoroethylene), PET (polyethylene terephthalate), POM (polyacetal), PA (polyamide), UHMW-PE (ultra high molecular weight polyethylene), PP (polypropylene), PE (polyethylene), HDPE (high density polyethylene), LDPE (low density polyethylene) and advanced engineering resins such as PBI (polybenzimidizole) and PAI (poly(amide-imide), PI (poly imide), PES (polyether sulfone), PAI (polyamide-imide), PAS (polyaryl sulfone) and as well as blends, co-polymers thereof. Such compositions may be made by compounding the polymers, or through other techniques such as reactive extrusion, co-extrusion, etc. for example.

"LCP (liquid crystal polymers), PEN (polyethylene naphthalate), PPL (polyphenylenes)"

E. Other Additives To The Blend

In addition to the polymer component of the blend, other beneficial compositions may be added to produce an improved article of manufacture. The skilled artisan will appreciate the wide range of ingredients which can be added to polymers to improve one or more manufacturing or performance property.

In some cases a metal oxide may be added to the polymers of the present invention. In some instances the metal oxide may further improve flame resistance (FR) performance by decreasing heat release and increasing the time to peak heat release. Titanium dioxide is of note. Other metal oxides include zinc oxides, boron oxides, antimony oxides, iron oxides and transition metal oxides. Metal oxides that are white may be desired in some instances. Metal oxides may be used alone or in combination with other metal oxides. Metal oxides may be used in any effective amount, in some instances at from 0.01 to about 20 wt% of the polymer blend.

Other useful additives include smoke suppressants such as metal borate salts for example zinc borate, alkali metal or alkaline earth metal borate or other borate salts. Additionally other of boron containing compounds, such as boric acid, borate esters, boron oxides or other oxygen compounds of boron may be useful. Additionally other

flame retardant additives, such as aryl phosphates and brominated aromatic compounds, including polymers containing linkages made from brominated aryl compounds, may be employed. Examples of halogenated aromatic compounds, are brominated phenoxy resins, halogenated polystyrenes, halogenated imides, brominated polycarbonates, brominated epoxy resins and mixtures thereof.

Conventional flame retardant additives, for example, phosphate esters, sulfonate salts and halogenated aromatic compounds may also be employed. Mixtures of any or all of these flame retardants may also be used. Examples of halogenated aromatic compounds are brominated phenoxy resins, halogenated polystyrenes, halogenated imides, brominated polycarbonates, brominated epoxy resins and mixtures thereof. Examples of sulfonate salts are potassium perfluoro butyl sulfonate, sodium tosylate, sodium benzene sulfonate, sodium dichloro benzene sulfonate, potassium diphenyl sulfone sulfonate and sodium methane sulfonate. In some instances sulfonate salts of alkaline and alkaline earth metals are preferred. Examples of phosphate flame retardants are tri aryl phosphates, tri cresyl phosphate, triphenyl phosphate, bisphenol A phenyl diphosphates, resorcinol phenyl diphosphates, phenyl-bis- (3,5,5'-trimethylhexyl phosphate), ethyl diphenyl phosphate, bis(2-ethylhexyl)-p-tolyl phosphate, bis(2-ethylhexyl)-phenyl phosphate, tri(nonylphenyl)phosphate, phenyl methyl hydrogen phosphate, di(dodecyl)-p-tolyl phosphate, halogenated triphenyl phosphates, dibutyl phenyl phosphate, 2-chloroethyldiphenyl phosphate, p-tolyl bis(2,5,5'-trimethylhexyl) phosphate, 2-ethylhexyldiphenyl phosphate, diphenyl hydrogen phosphate, resorcinol diphosphate and the like. In some instances it maybe desired to have flame retardant compositions that are essentially free of halogen atoms, especially bromine and chlorine. Essentially free of halogen atoms means that in some embodiments the composition has less than about 3% halogen by weight of the composition and in other embodiments less than about 1% by weight of the composition containing halogen atoms. The amount of halogen atoms can be determined by ordinary chemical analysis. The composition may also optionally include a fluoropolymer in an amount of 0.01 to about 5.0 % fluoropolymer by weight of the composition. The fluoro polymer may be used in any effective amount to provide anti-drip properties to the resin composition. Some possible examples of

suitable fluoropolymers and methods for making such fluoropolymers are set forth, for example, in US Patents 3,671,487, 3,723,373 and 3,383,092. Suitable fluoropolymers include homopolymers and copolymers that comprise structural units derived from one or more fluorinated alpha-olefin monomers. The term "fluorinated alpha-olefin monomer" means an alpha-olefin monomer that includes at least one fluorine atom substituent. Some of the suitable fluorinated alpha-olefin monomers include, for example, fluoro ethylenes such as, for example, $CF_2=CF_2$, $CHF=CF_2$, $CH_2=CF_2$ and $CH_2=CHF$ and fluoro propylenes such as, for example, $CF_3CF=CF_2$, $CF_3CF=CHF$, $CF_3CH=CF_2$, $CF_3CH=CH_2$, $CF_3CF=CHF$, $CHF_2CH=CHF$ and $CF_3CF=CH_2$.

Some of the suitable fluorinated alpha-olefin copolymers include copolymers comprising structural units derived from two or more fluorinated alpha-olefin monomers such as, for example, poly(tetrafluoro ethylene-hexafluoro ethylene), and copolymers comprising structural units derived from one or more fluorinated monomers and one or more non-fluorinated monoethylenically unsaturated monomers that are copolymerizable with the fluorinated monomers such as, for example, poly(tetrafluoroethylene-ethylene-propylene) copolymers. Suitable non-fluorinated monoethylenically unsaturated monomers include for example, alpha-olefin monomers such as, for example, ethylene, propylene, butene, acrylate monomers such as for example, methyl methacrylate, butyl acrylate, and the like, with poly(tetrafluoroethylene) homopolymer (PTFE) preferred.

The blends may further contain fillers and reinforcements for example fiber glass, milled glass, glass beads, flake and the like. Minerals such as talc, wollastonite, mica, kaolin or montmorillonite clay, silica, quartz and barite may be added. The compositions can also be modified with effective amounts of inorganic fillers, such as, for example, carbon fibers and nanotubes, metal fibers, metal powders, conductive carbon, and other additives including nano-scale reinforcements. Other fillers well known to the skilled artisan, which may be conductive, may be employed to have the connector of the present invention provide shielding.

Other additives include, antioxidants such as phosphites, phosphonites and hindered phenols. Phosphorus containing stabilizers including triaryl phosphite and aryl phosphonates are of note as useful additives. Difunctional phosphorus containing compounds can also be employed. Stabilizers with a molecular weight of greater than or equal to about 300 are preferred. In other instances phosphorus containing stabilizers with a molecular weight of greater than or equal to 500 are useful. Phosphorus containing stabilizers are typically present in the composition at 0.05-0.5% by weight of the formulation. Colorants as well as light stabilizers and UV absorbers may also be present in the blend. Flow aids and mold release compounds are also contemplated. Examples of mold release agents are alkyl carboxylic acid esters, for example, pentaerythritol tetrastearate, glycerin tristearate and ethylene glycol distearate. Mold release agents are typically present in the composition at 0.05-0.5% by weight of the formulation. Preferred mold release agents will have high molecular weight, typically greater than about 300, to prevent loss of the release agent from the molten polymer mixture during melt processing.

Additives which may be used in the present invention include impact modifiers comprising three polymers wherein one polymer has as an acid component may also be used. Non-limiting examples are acrylic acid-butadiene-styrene copolymer, carbonic acid-butadiene-styrene copolymer or an acid compound containing carbonic acid anhydride-butadiene-styrene copolymer. Impact modifiers having a rubbery component that comprises polyolefins such as ethylene or propylene can also be used. Copolymers of ethylene and propylene can also be used. Rubbery components such as a polyolefin containing an acid modified component such as butadiene or a reactive epoxy functionality may also be used.

Fibrous fillers having aspect ratios from 2 to 1000 maybe used to impart strength to the composition. Non-limiting examples of such fibers are glass fibers, hollow glass fibers, carbon fibers, hollow carbon fibers, titanium oxide whiskers, and wollastonite. Non-fibrous fillers may also be utilized to impart strength and dimensional stability to the pipe. Such fillers may exist is in the form of platelets, particles which may be crystalline or amorphous. Non-limiting examples of such non-fibrous fillers arc talc, clay, silica, glass flakes, glass beads, hollow filler etc. Combinations of fibrous and

non-fibrous fillers may also be used. Impact modifiers may generally be used in the pipe composition in an amount of up to about 7 wt % based on the total weight of the composition.

In addition to being added as impact modifiers, polyolefins may be added to modify the chemical resistance characteristics and mold release characteristics of the composition. Homo polymers such as polyethylene, polypropylene, polybutene can be used either separately or in combination. Polyethylene can be added as high density polyethylene (HDPE), low density polyethylene (LDPE) or branched polyethylene. Polyolefins may also be used in copolymeric form with compounds containing carbonic acid radicals such as maleic acid or citric acid or their anhydrides, acid compounds containing acrylic acid radicals such as acrylic acid ester, and the like, as well as combinations comprising at least one of the foregoing.

Alicyclic, saturated hydrocarbon resins such as those available from hydrogenation of aromatic hydrocarbon resin, for example generally, C_9 hydrocarbon resin, C_5/C9 hydrocarbon resin, indene-chroman resin, vinyl aromatic resin, terpene-vinyl aromatic resin and the like may also be used. With respect to the terpene variety, terpene resins formed by using .alpha.-pinene, .beta.-pinene, and diterpenes as the raw material is preferred. Terpene denatured by aromatic hydrocarbon (phenol, bisphenol A, and the like) or hydrogen-saturated terpenes, and the like are also useful. With regards to the petroleum hydrocarbons, a liquid fraction of petroleum fraction is appropriate for use. Similarly with regards to the aromatic hydrocarbon petroleum resin, aromatic hydrocarbon fraction polymer represented by C9 carbon variety is used. The hydrogen addition ratio is desired to be high, preferably at least about 30%. If the quantity of aromatic component is greater, then desirable properties may be lost.

Thermal stabilizers, which increase the thermal stability of the composition, may also be added. Such compounds include phosphite stabilization agents, epoxy compounds, beta-diketone, inorganic stabilizers such as perchloric acid salts, talc, zeolite and the like, as well as combinations comprising at least one of the foregoing thermal stabilizers. Preferred phosphite stabilization agents are tri alkyl phosphite, alkyl aryl phosphite, tri aryl phosphite and combinations comprising at least one of the

foregoing phosphite stabilization agents. Thermal stabilizers may be added in quantities of greater than or equal to about 0.01, preferably greater than or equal to about 0.1 parts by weight based on 100 parts of weight of polyphenylene ether resin and polystyrene resin. It is also generally desirable to add thermal stabilizers in quantities of less than or equal to about 70, preferably less than or equal to about 50 parts by weight based on 100 parts of weight of polyphenylene ether resin and polystyrene resin.

Drip prevention agents such as those that prevent dripping during combustion, may also be utilized. Polytetrafluoroethylene is preferred as a drip prevention agent because of its ability to form fibrils in the composition. Other drip prevention agents, which can form fibrils, are also preferred. Drip prevention agents may be added in quantities of about 0.01 to about 5 parts by weight based on 100 parts of weight of polyphenylene ether resin and polystyrene resin. Within this range it is preferable to use the drip prevention agent in an amount of greater than or equal to about 0.05 by weight based on 100 parts of weight of polyphenylene ether resin and polystyrene resin. Within this range, it is also generally desirable to add the drip prevention agents in quantities of less than or equal to about 3 parts by weight based on 100 parts of weight of polyphenylene ether resin and polystyrene resin.

Polymer blends used in articles according to the present invention may also include various additives such as nucleating, clarifying, stiffness and/or crystallization rate agents. These agents are used in a conventional matter and in conventional amounts.

Methods For Making Blends According to the Present Invention

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 compositions and articles of the invention.

The polymer blends according to the present invention, can also be shaped or fabricated into elastic films, coatings, sheets, strips, tapes, ribbons and the like. The elastic film, coating and sheet which may be used to make the annular shapes of the present invention may be fabricated by any method known in the art, including blown bubble processes (e.g., simple bubble as well as biaxial orientation techniques such trapped bubble, double bubble and tenter framing), cast extrusion, injection molding processes, thermoforming processes, extrusion coating processes, profile extrusion, and sheet extrusion processes.

Compression molding is well known to the skilled artisan, wherein the polymer blend is placed in a mold cavity or into contact with a contoured metal surface. Heat and/or pressure, by for example, a hydraulic press, are then applied to the polymer blend for a given time, pressure and temperature, with the conditions being variable depending on the nature of the blend. Pressure from the molding tool forces the polymer blend to fill the entire mold cavity. Once the molded article is cooled, it can be removed from the mold with the assistance of an ejecting mechanism. Upon completion of the process, the polymer blend will have taken the form of the mold cavity or the contoured metal surface. U.S. Patent 4,698,001 to Visamara discloses methods of performing compression molding.

Injection molding is the most prevalent method of manufacturing for non-reinforced thermoplastic parts, and is also commonly used for short-fiber reinforced thermoplastic composites. Injection molding can be used to produce articles according to the present invention. Injection molding is a process wherein an amount of polymer blend several times that necessary to produce an article is heated in a heating chamber to a viscous liquid and then injected under pressure into a mold cavity. The polymer blend remains in the mold cavity under high pressure until it is cooled and is then removed. Injection molding and injection molding apparatus are discussed in further detail in U.S. Patents 3,915,608 to Hujick; 3,302,243 to Ludwig; and 3,224,043 to Lameris. Injection molding is generally used for large volume applications such as

automotive and consumer goods. The cycle times range between 20 and 60 seconds. Injection molding also produces highly repeatable near-net shaped parts. The ability to mold around inserts, holes and core material is another advantage. The skilled artisan will know whether injection molding is the best particular processing method to produce a given article according to the present invention.

Blow molding is a technique for production of hollow thermoplastic products. Blow molding involves placing an extruded tube of a thermoplastic polymer according to the present invention, in a mold and applying sufficient air pressure to the inside of the tube to cause the outside of the tube to conform to the inner surface of the die cavity. U.S. patent 5,551,860 describes a method of performing blow molding to produce an article of manufacture in further detail. Blow molding is not limited to producing hollow objects. For example a "housing" may be made by blowing a unit and then cutting the unit in half to produce two housings. Simple blown bubble film processes are also described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192.

Oriented films may be prepared through blown film extrusion or by stretching cast or calendered films in the vicinity of the thermal deformation temperature using conventional stretching techniques. For instance, a radial stretching pantograph may be employed for multi-axial simultaneous stretching; an x-y direction stretching pantograph can be used to simultaneously or sequentially stretch in the planar x-y directions. Equipment with sequential uniaxial stretching sections can also be used to achieve uniaxial and biaxial stretching, such as a machine equipped with a section of differential speed rolls for stretching in the machine direction and a tenter frame section for stretching in the transverse direction.

Thermoplastic molding system includes a thermoplastic extrusion die for the extrusion of a thermoplastic slab profiled by adjustable die gate members, i.e., dynamic die settings, for varying the thickness of the extruded material in different parts of the extruded slab. The thermoplastic extrusion die has a trimmer for cutting the extruded thermoplastic slab from the thermoplastic extrusion die. A plurality of

thermoplastic molds, which may be either vacuum or compression molds, are each mounted on a movable platform, such as a rotating platform, for moving one mold at a time into a position to receive a thermoplastic slab being trimmed from the thermoplastic extrusion die. A molded part is formed with a variable thickness from a heated slab of thermoplastic material being fed still heated from the extrusion die. A plurality of molds are mounted to a platform to feed one mold into a loading position for receiving a thermoplastic slab from the extrusion die and a second mold into a release position for removing the formed part from the mold. The platform may be a shuttle or a rotating platform and allows each molded part to be cooled while another molded part is receiving a thermoplastic slab. A thermoplastic molding process is provided having the steps of selecting a thermoplastic extrusion die setting in accordance with the apparatus adjusting the thermoplastic extrusion die for varying the thickness of the extruded material passing there through in different parts of the extruded slab. The thermoplastic material is heated to a fluid state and extruded through the selected thermoplastic die which has been adjusted for varying the thickness of the extruded material in different parts of the extruded slab, trimming the extruded thermoplastic slab having a variable thickness to a predetermined size, and directing each trim slab of heated thermoplastic material onto a thermoforming mold, and molding a predetermined part in the mold so that the molded part is formed with a variable thickness from a slab of material heated during extrusion of the material. Injection molding, thermoforming, extrusion coating, profile extrusion, and sheet extrusion processes are described, for example, in Plastics Materials and Processes, Seymour S. Schwartz and Sidney H. Goodman, Van Nostrand Reinhold Company, New York, 1982, pp. 527-563, pp. 632-647, and pp. 596-602.

Vacuum molding may be used to produce shaped articles of manufacture according to the present invention. In accordance with this method, a sheet of a polymeric material according to Formula 1 is fixed by means of iron frames or other device, fitted to a jig that makes easy handling, and then introduced into an apparatus where it is heated by means of ceramic heaters or wire heaters arranged at upper and lower positions. The sheet starts to melt on heating. On continuing the heating after sagging of the sheet once occurred, the sheet is stretched in the frame. Upon observation of such

stretching, the sheet can be molded with uniform thickness and no wrinkles or other defects. At this point, the sheet frame is taken out of the heating apparatus, positioned next to a mold, and vacuum molded under a reduced pressure of 1 atmospheric pressure, whereupon the desired mold shaped article can be obtained. Thereafter, the article can be cooled with air or sprayed water and taken out of the mold.

In accordance with pressure molding, a sheet which has been heated or which otherwise has become easy to handle is placed on a mold, pressure is applied to the sheet such that the sheet takes the shape of a mold, through the application of pressure.

An article of manufacture comprising a resin according to formula I may also be made using a stamp molding process. For example, a shaped piece of polymer of Formula I in a squeezing mold fitted to a vertical press machine and then heat molded under a pressure of from 5 to 500 kg/cm^2 (preferably from 10 to 20 kg/cm2) whereupon the desired shaped article. The mold is then cooled with air or sprayed water and the article is taken out of the mold. In this molding, the press time is usually at least 15 seconds, and generally from 15 to 40 seconds. In order to improve surface characteristics, it is preferred that the molding be performed under two-stage pressure conditions. At the first stage, the polymer material is maintained under a pressure of from 10 to 20 kg/cm.sup.2 for from 15 or 40 seconds. Then a second stage pressure of from 40 to 50 kg/cm.sup.2 for at least 5 seconds, whereupon a molded article having superior surface smoothness can be produced. This method can be preferred when an inorganic filler-containing thermoplastic resin according to Formula I having poor fluidity is used.

The well known process of injection molding can also be used to produce articles of manufacture using resins having formula I. Injection molding is where resin is injected into a mold cavity under pressure. The injection pressure is usually from 40 to 140 kg/cm^2 and preferably from 70 to 120 kg/cm^2.

PIPE

Polymers according top the present invention may be used for pipe and pipe applications, including, but not limited to pipe joints, adapters, etc. Any variety of pipe known in the art may be made according to the present invention. This includes, heat pipe for the absorption and/or radiation of heat for heat transfer application, conduit pipe for moving liquids and/or solids from one location to another, fire resistant pipe for aerospace applications, flexible or rigid pipes for under the hood or other automotive applications, threaded pipe, high pressure pipe and fiber reinforced pipe.

In one embodiment, the melt blending of the polymers and blends and any other additives, necessary or desirable to improve the properties of the pipe, may be compounded in an extruder by adding the components simultaneously at the throat or sequentially through different feeders located at different positions along the barrel of the extruder. The extrudate emanating from the extruder may be either fed directly to a molding machine or cooled and converted into pellets, powder, and the like for use in a future molding operation to make the pipe sections. Alternatively, the pipe may be molded by feeding the components, and additives, directly into the molding machine, where the components may be mixed immediately prior to molding. The polymer and/or blend can also be melt blended and subsequently molded into a pipe. Melt blending operations are generally carried out in an extruder, ball mixer, roll mill, buss kneader and the like. During the melt blending operation, a small quantity of solvent may be added to the melt to facilitate processing if desired. During melt blending, the various components may be added simultaneously or sequentially if desired.

The pipe may be molded from pellets, powder, and the like by methods such as injection molding, extrusion molding, blow molding, vacuum forming, and any other molding operations known in the art. Both straight pipe sections as well as pipe joints may be molded, Extrusion molding is generally preferred for straight sections while injection molding is preferred for molding joints. While pipe diameter, wall thicknesses, and shape may be chosen as desired, a preferred wall thickness is from

about 2.0 to about 500 or from 2.0 to about 100 or from about 2.0 to about 50 or from about 2.0 to about 10 millimeters (mm). Pipe profiles may vary from cylindrical to quadrilateral to hexagonal, with cylindrical shapes generally being preferred.

Pipes made from polymers and blends described herein may also be constructed in multi-layered or laminated form comprising at least two layers. Multilayered pipes may be constructed utilizing as many layers as may be desired so long as they are thermally stable and have water proof properties. When a pipe has two or more layers, it is desirable that at least one layer be constructed from the composition comprising polyphenylene ether resin and polystyrene resin.

Pipes made for water transmission and distribution, may be made to display thermal stability, strength and ability to withstand high pressures in measures similar to PVC pipe. Further no cracks and fissures were seen in the flatness test, which indicates the excellent pressure resistance characteristics of the composition. Pipes made from the above-described composition are also advantageous in that they do not contain components such as lead, which may be transmitted by the water. Further other detrimental factors such as increase in muddiness, color change, odor absorption, loss of taste, and the like, normally associated with steel pipes does not occur. Additionally, since the pipe does not contain any PVC, chlorine does not get into the water from the pipe.

Several U.S. patents which provide some detail as to the state of the art in the art of methods of making pipes and pipes so made are: 6,942,016; 6,920,900; 6,905,150; 6,840,202.

Pipe may be made using the polymer materials mentioned herein. For example, pipe having two openings and

TUBING

The polymer compositions described herein can be used to form tubing for tubing applications requiring high heat and/or chemical resistance. For example, in oil well applications, tubing can be used to convey and/or cover probes and sensors into a

well. Tubing according to the present invention may also be employed to convey chemicals and/or hot materials, in for example, liquid form. Methods of making and using tubing are described for example, in U.S. Patents: 4,374,530; 4,345,363; 4,346,737; 4,199,314; 4,109,365 and, 6,863,852.

WIRE COATING

The polymer compositions of the present invention can also be employed as wire coat or bead coat compounds. For example, it can be used for wire coat in hose, belts and, in particular, tires. Such pneumatic tires can be built, shaped, molded and cured by various methods which are known and will be readily apparent to those having skill in such art. As can be appreciated, the tire may be a passenger tire, aircraft tire, truck tire and the like. Polymer compositions according to the claimed invention may also be used to coat wire and cable, such as for example, copper wire and any form of metal cable.

Methods of coating a wire which may be used according to the present invention are well known in the art and are discussed for example in U.S. Patents: 4,588,546 to Feil et al.; 4,038,237 to Snyder et al.; 3,986,477 to Bigland et al.; and, 4,414,355 to Pokorny et al.

The wire coating of this invention is typically about 0.1 to about 40 mils (2.5 to 1000 .mu.m) thick, preferably about 1 to about 20 mils (25 to 500 .mu.m) thick, and more preferably about 2 to about 10 mils (50 to 250 .mu.m) thick, and most preferably about 4 to about 7 mils (100 to 175 .mu.m) thick.

It is desirable that wire coating have as few lumps and sparks as possible. Coated wire made according to the teachings of this invention may have fewer than about 10 lumps/135,000 ft (41,000 m) and fewer than about 10 sparks/135,000 ft (41,000 m), preferably fewer than about 5 lumps /135,000 ft (41,000 m) and fewer than about 5 sparks/135,000 ft (41,000 m), and more preferably fewer than about 2 lumps/135,000 ft (41,000 m) and may have no more than about 2 sparks/135,000 ft (41,000 m).

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 1

FORMULATIONS 1-9

Some properties are measured using ASTM test methods. All molded samples are conditioned for at least 48h at 50% relative humidity prior to testing. Reverse notched Izod impact values are measured at room temperature on 3.2 mm thick bars as per ASTM D256. Heat distortion temperature (HDT) is measured at 0.46 MPa (66 psi) on 3.2 mm thick bars as per ASTM D648. Tensile properties are measured on 3.2 mm type I bars as per ASTM method D638. Flexural properties are measured on 3.2 mm bars as per ASTM method D790. Vicat temperature is measured at 50N as per ASTM method D1525. Differential scanning calorimetry (DSC) is run as per ASTM method D3418, but using different heating and cooling rates. Samples are heated at 20 °C/min to 350 °C and cooled at either 20 or 80 °C/min. to record peak crystallization temperature (Tc). Dynamic Mechanical Analysis (DMA) is run in flexure on 3.2 mm bars at a heating rate of 3 °C/min. with an oscillatory frequency of at 1 Hertz. DMA tests are run from about 30 to about 300 °C as per ASTM method D5418. Viscosity vs. shear rate is measured on a capillary rheometer using a 1x10 mm die at 380 °C as per ASTM method D3835. Pellets of the blends are dried at 150 °C for at least 3 hrs before testing using a parallel plate rheometer at 10 radians/min. the change in melt viscosity at 380 °C is measured vs. time.

Glass transition temperatures (Tgs) can be measured by several techniques known in the art, for example ASTM method D34318. In measuring Tg different heating rate

can be employed , for example from 5 to 30 °C per minute or in other instances from 10 to 20 °C per minute.

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. Determinations of 20° gloss, CIE L* value, and appearance are performed for each sample as molded. Twenty degree gloss are measured according to ASTM D523 using a black tile standard. CIE lightness (L*) values are measured as described in R. McDonald (ed.), "Colour Physics for Industry, Second Edition" The Society of Dyers and Colourists, Bradford, UK (1997). Appearance refers to a subjective visual examination of the color and translucency/opacity of the as molded parts.

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 2

Inventive formulations 1, 2, 3, 4 and 5, above, are injection molded into pipe sections and pipe connectors using one or more of the techniques described above.

EXAMPLE 3

Material made according to formulations 6, 7, 8 and 9 of table 1 are injection molded into a mold cavity to form pipe sections.

EXAMPLE 4

FORMULATIONS 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. Test samples are injection molded at a set temperature of 320-360 °C and mold temperature of 120 °C using a 30 sec. cycle time.

Table 2

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

Material made according to formulations 10 and 11 are injection molded into a mold cavity in the form pipe sections.

EXAMPLE 5

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

Formulations 12-18 are each are extruded to form 2 mm tubing.

EXAMPLE 6

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			

Inventive formulations 19-25, above, are co-etruded over copper wire for use as a wire coating using one or more of the techniques described above.

EXAMPLE 7

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

Formulations 26-31 are each injection molded into a mold cavity in the form of a large annular shape for use to connect pipe sections.

EXAMPLE 8

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

Examples *	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

Formulations 32-34 are injection molded at a set temperature of 320-360 °C and mold temperature of 120 °C using a 30 sec. cycle time to form pipe sections.

EXAMPLE 9

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

Examples *	35	36
PSu	37.5	0
PES	0	37.5
PEI Siloxane	2.5	2.5
ITR9010	60	60

* blends had 3 phr TiO2

Formulations 35-36 are co-extruded with copper wire at a set temperature of 320-360 °C to form a coated wire.

All aforementioned patents and patent applications are herein specifically incorporated by reference in their entirety as though set forth in full.

While the invention has been described with reference to preferred embodiments, it will be understood by those skilled in the art that various changes may be made, and equivalents substituted, for elements thereof without departing from the scope of the

invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiments disclosed as the best mode contemplated for carrying out the present invention, but that the invention will include all embodiments falling within the scope of the appended claims.

WHAT IS CLAIMED IS:

1. A tubular article of manufacture in an annular or tubular shape having an outer diameter, an inner diameter and a length comprising one or more materials selected from the group consisting of: 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. A tubular article of manufacture according to claim 1 wherein the polyetherimide has a hydrogen atom to carbon atom ratio of between about 0.4 and 0.85.

3. A tubular article of manufacture according to claim 1 wherein the polyetherimide is essentially free of benzylic protons.

4. A tubular article of manufacture according to claim 1 wherein the outer diameter of the article is substantially the same throughout the length.

5. A tubular article of manufacture according to claim 1 wherein the inner diameter of the article is substantially the same throughout the length.

6. A tubular article of manufacture according to claim 1 wherein the difference between the outer diameter and the inner diameter of the article is substantially the same throughout the length.

7. A tubular article of manufacture according to claim 1 wherein the tubular article comprises a coating on a shaped article having a different composition than the coating.

8. A tubular article of manufacture according to claim 5 wherein the article takes the form of a coating on a solid metal wire.

9. A tubular article of manufacture according to claim 5 wherein the article takes the form of a coating on a hollow tube.

10. A tubular article of manufacture according to claim 5 wherein the article takes the form of a coating on a solid cable core.

11. A tubular article of manufacture according to claim 5 wherein the article takes the form of a paint coating on a solid or hollow core.

12. A tubular article of manufacture according to claim 5 wherein the article takes the form of a pipe.

13. A tubular article of manufacture according to claim 5 wherein the article is a coating over a means for transmitting an electronic current or signal.

14. A tubular article of manufacture according to claim 1, wherein one or more of the resins is in the form of a foam.

15. A tubular article of manufacture according to claim 1, wherein the article takes the form tubing.

16. A tubular article of manufacture according to claim 1, wherein the article takes the form of a hollow fiber.

17. A tubular article of manufacture according to claim 1, wherein the article takes the form of an insulating coating over a shaped article.

18. A tubular article of manufacture according to claim 1, wherein the article takes the form of an insulating coating over a shaped article wherein the coating acts as a thermal or electrical insulator.

19. A tubular article of manufacture according to claim 1 comprising an immiscible blend of polymers having more than one glass transition temperature and wherein the non-polyetherimide polymer has a glass transition temperature greater than about 180° Celsius.

20. A tubular article of manufacture according to claim 1 comprising a miscible blend of polymers having a single glass transition temperature greater than 200° Celsius.

21. A tubular article of manufacture according to claim 1 comprising a single polyetherimide polymer having a glass transition temperature of greater than 247° Celsius.

22. A tubular article of manufacture 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.

23. A tubular article of manufacture according to claim 22 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.

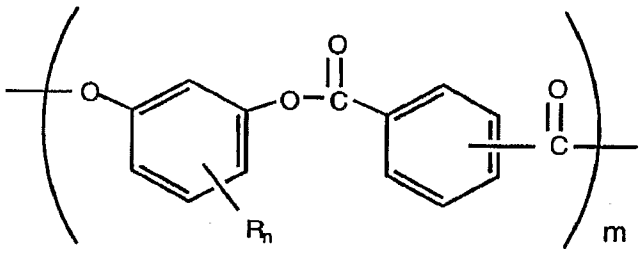
24. A tubular article of manufacture according to claim 22 wherein the silicone copolymer content is from 0.1 to about10.0 wt% of the polymer blend.

25. A tubular article of manufacture according to claim 22 wherein the silicone copolymer has from 5 to about 70 wt% siloxane content.

26. A tubular article of manufacture according to claim 22 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.

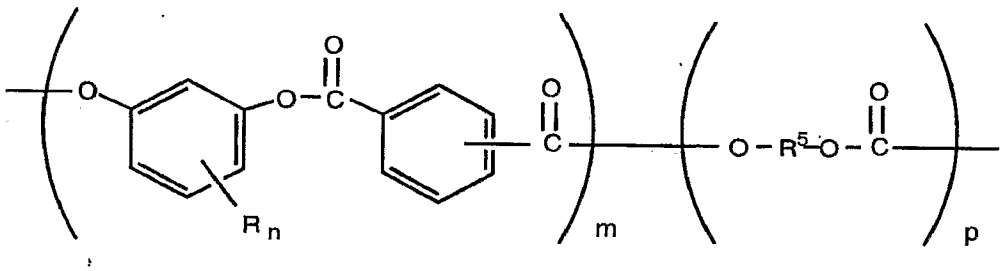
27. A tubular article of manufacture according to claim 1 further comprising one or more metal oxides at 0.1 to 20% by weight of polymer.

28. A tubular article of manufacture according to claim 22 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.

29. A tubular article of manufacture according to claim 22 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.

30. A tubular article of manufacture according to claim 29 wherein R^5 is derived from a bisphenol compound.

31. A tubular article of manufacture according to claim 1 wherein the immiscible, phase separated, polymer blend 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.

32. A tubular article of manufacture according to claim 31 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.

33. A tubular article of manufacture according to claim 31 wherein at least 50 mole% of the polysulfone etherimide linkages are derived from oxydiphthalic anhydride or a chemical equivalent thereof.

34. A tubular article of manufacture according to claim 31 wherein less than 30 mole% of polysulfone etherimide linkages are derived from a diamine or dianhydride containing an isoalkylidene group.

35. A tubular article of manufacture according to claim 1 wherein the article 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.

36. A tubular article of manufacture according to claim 31 wherein the polysulfone etherimide is present from 30 to about 70 wt% of the article.

37. A tubular article of manufacture according to claim 31 wherein the article has a modulus of greater than about 200 Mpa at 200 °C, as measured by ASTM D5418, on a 3.2 mm sample.

38. A tubular article of manufacture according to claim 31 wherein the polysulfone etherimide is essentially free of benzylic protons.

39. A tubular article of manufacture according to claim 31 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.

40. A tubular article of manufacture according to claim 38 wherein the polysulfone etherimide has a glass transition temperature (Tg), from 250° to 350 °C.

41. A tubular article of manufacture according to claim 1 comprising a polymer blend having at least two different glass transition temperatures, as measured by ASTM method D5418, wherein the first glass transition temperature is from 120° to 200 °C and the second glass transition temperature is from 250° to 350 °C.

42. A tubular article of manufacture 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.

43. A tubular article of manufacture according to claim 42 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.

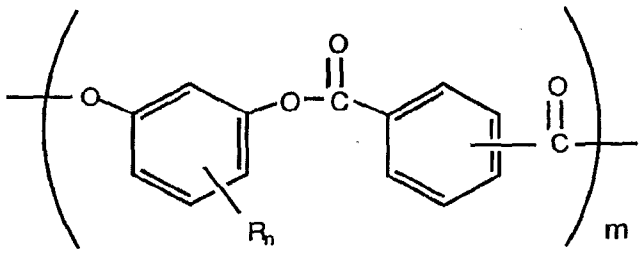
44. A tubular article of manufacture according to claim 42 wherein the silicone copolymer content is from 0.1 to about 10.0 wt% of the polymer blend.

45. A tubular article of manufacture according to claim 42 wherein the silicone copolymer has from 5 to 70 wt% siloxane content.

46. A tubular article of manufacture according to claim 42 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.

47. A tubular article of manufacture according to claim 1 further comprising one or more metal oxides at 0.1 to 20% by weight of the polymer blend.

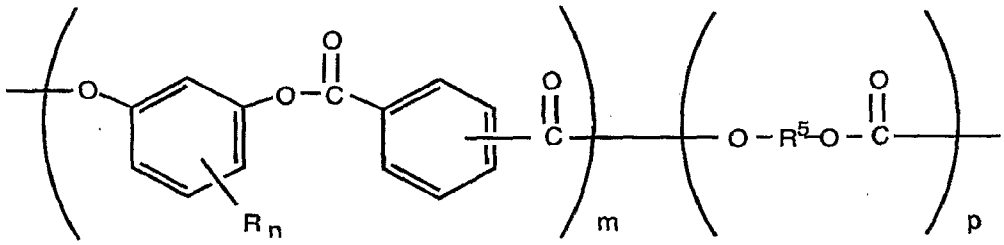
48. A tubular article of manufacture according to claim 42 wherein the resorcinol based aryl polyester has the structure shown below:



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.

49. A tubular article of manufacture according to claim 42 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.

50. A tubular article of manufacture according to claim 49 wherein R^5 is derived from a bisphenol compound.

51. A tubular article of manufacture according to claim 42 wherein the polyetherimide is made from

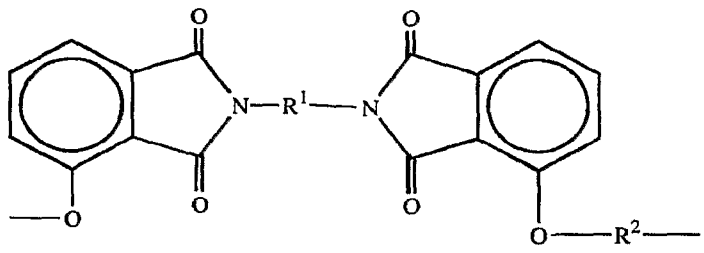
(a) aryl dianhydrides selected from the group consisting of: bisphenol A dianhydride, oxydiphthalic anhydride, pyromellitic dianhydride, diphthalic anhydride,

sulfonyl dianhydride, sulfur dianhydride, benzophenone dianhydride and mixtures thereof; and,

(b) 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.

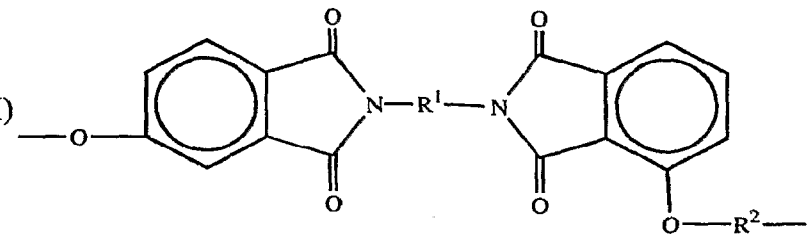
52. A tubular article of manufacture according to claim 1 wherein the article comprises a copolyetherimide having a glass transition temperature of at least about 218°C, said copolyetherimide comprising structural units of the formulas (I) and

(I)



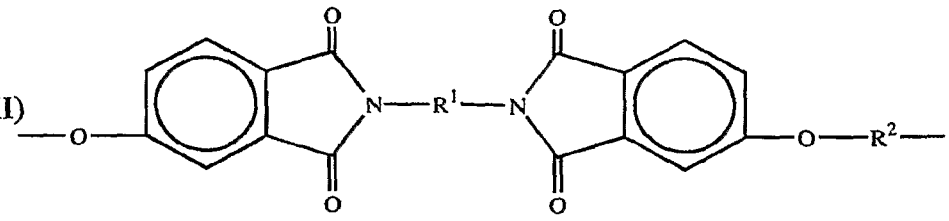
(II):

(II)



and optionally structural units of the formula (III):

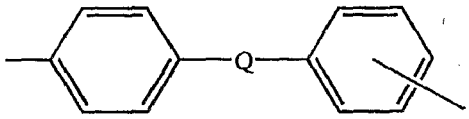
(III)



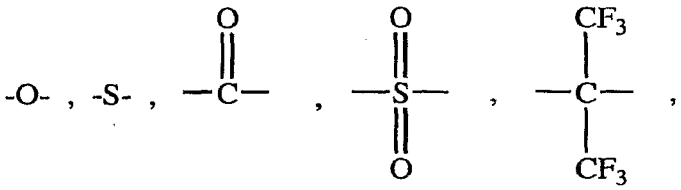
,

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.

53. A tubular article of manufacture according to claim 52 comprising a copolyetherimide having a Tg greater than 225°C.

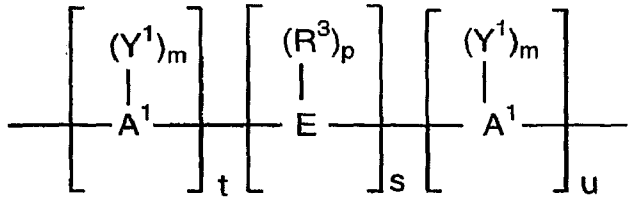
54. A tubular article of manufacture according to claim 52 comprising a copolyetherimide comprising structural units of the formula (III).

55. A tubular article of manufacture according to claim 52 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-phenylene-diamine; 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.

56. A tubular article of manufacture according to claim 52 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.

57. A tubular article of manufacture according to claim 52 wherein R^2 structural units in each of formulas (I), (II) and (III) are the same.

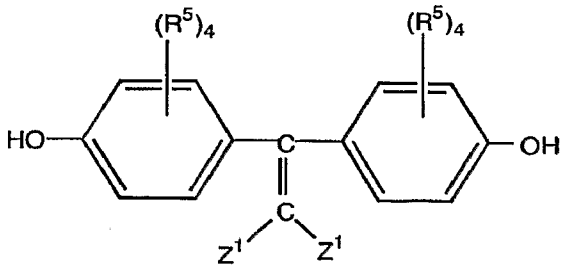
58. A tubular article of manufacture according to claim 52 wherein at least a portion of R^2 structural units in at least two of formulas (I), (II) and (III) are not the same.

59. A tubular article of manufacture according to claim 52 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)sulfide; 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)sulfide, 3-(4-hydroxyphenyl)-1,1,3-trimethylindan-5-ol, 1-(4-hydroxyphenyl)-1,3,3-trimethylindan-5-ol, 2,2,2',2'-tetrahydro-3,3,3',3'-tetramethyl-1,1'-spirobi[1H-indene]-6,6'-diol.

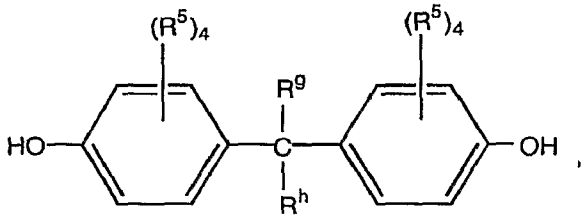
60. A tubular article of manufacture according to claim 52 wherein R^2 is derived from at least one dihydroxy-substituted aromatic hydrocarbon selected from the group consisting of those of the formula (IX):

(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^l is chlorine or bromine; and those of the formula (X):

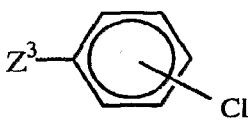
(X) 

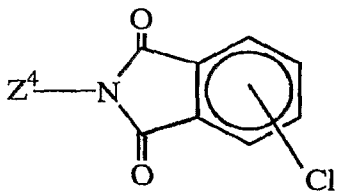
where independently each R^5 is as defined hereinbefore, and independently R^g and R^h are hydrogen or a C_{1-30} hydrocarbon group.

61. A tubular article of manufacture according to claim 52 wherein R^2 is derived from bisphenol A.

62. A tubular article of manufacture according to claim 52 further comprising structural units derived from at least one chain termination agent.

63. A tubular article of manufacture according to claim 62 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.

64. A tubular article of manufacture according to claim 62 wherein the chain termination agent is at least one member selected from the group consisting of monochloro benzophenone, monochloro diphenylsulfone; a monochloro phthalimide; 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 monochloro bisphthalimidobenzene; 1-[N-(4-chlorophthalimido)]-3-(N-phthalimido)benzene; 1-[N-(3-chlorophthalimido)]-3-(N-phthalimido)benzene; monochloro bisphthalimido diphenyl sulfone, monochloro bisphthalimido diphenyl ketone, a monochloro bisphthalimido phenyl 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.

65. A tubular article of manufacture according to claim 52 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.

66. A tubular article of manufacture according to claim 52 which has a heat distortion temperature at 0.455 MPa of at least 205°C.

67. A tubular article of manufacture according to claim 52 which has a heat distortion temperature, as measured by ASTM method D648, at 0.455 MPa of at least 210°C.

68. A tubular article of manufacture according to claim 52 which has a temperature of transition between the brittle and ductile states of at most 30°C as measured by ASTM method D3763.

69. A tubular article of manufacture according to claim 52 wherein the polyetherimides has a weight average molecular weight, as determined by gel permeation chromatography relative to polystyrene standards, in the range of between about 20,000 and about 80,000.

70. A tubular article of manufacture according to claim 52 comprising a single polyetherimide having a glass transition temperature of greater than 247° Celsius.

71. A tubular article of manufacture according to claim 52 comprising a blend of polymers containing at least one polyetherimide having a glass transition temperature of greater than 217° Celsius.

72. A tubular article of manufacture according to claim 52 comprises a resin blend of: a) a first resin selected from the group consisting of: polysulfones, polyether sulfones, polyphenylene ether sulfones, and mixtures thereof; b) a second resin comprising a silicone copolymer; c) 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 together with; and, d) a fourth resin comprising one or more resins selected from the group consisting of polyarylethers, polycarbonates, polyestercarbonates, polyarylates, polyamides, and polyesters.

73. A tubular article of manufacture according to claim 52, comprises a single phase amorphous resin blend having one or more polymers selected from the group consisting of polyetherimides and single phase blends comprising polyesters and polyetherimides.

74. A tubular article of manufacture according to claim 1 further comprising a compound containing at least one boron atom.

75. A tubular article of manufacture according to claim 1 which has a two-minute peak heat release, as measured by FAR 25.853, of less than about 60 kW-min/m^2.

76. A tubular article of manufacture according to claim 1 which has a total heat release, as measured by FAR 25.853, of less than about 80 kW/m^2.

77. A tubular article of manufacture according to claim 1 wherein the article comprises a polymer blend having a tensile elongation at break, as measured by ASTM D638, of greater than or equal to about 50%.

78. A tubular article of manufacture according to claim 1 wherein the polymer blend has a flexural modulus, as measured by ASTM D790, of greater than or equal to about 300 Kpsi (2070 Mpa).

79. A tubular article of manufacture according to claim 1 wherein the article comprises: sheets, films, multilayer sheets, hollow fibers, films, multilayer films, molded parts, extruded profiles, coated parts and foams.

80. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 218° C or above.

81. A tubular article of manufacture according to claim 1 in which the electrical connector comprises a material which has at least one Tg of 219° C or above.

82. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 220° C or above.

83. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 221° C or above.

84. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 222° C or above.

85. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 223° C or above.

86. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 224° C or above.

87. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 225° C or above.

88. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 230° C or above.

89. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 235° C or above.

90. A tubular article of manufacture according to claim 1in which the article comprises a material which has at least one Tg of 240° C or above.

91. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 245° C or above.

92. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 250° C or above.

93. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 255° C or above.

94. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 260° C or above.

95. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 265° C or above.

96. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 270° C or above.

97. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 275° C or above.

98. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 300° C or above.

99. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 325° C or above.

100. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg of 350° C or above.

101. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg between about 225° C and 250° C.

102. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg between about 250° C and 275° C.

103. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg between about 275° C and 300° C.

104. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg between about 300° C and 325° C.

105. A tubular article of manufacture according to claim 1 in which the article comprises a material which has at least one Tg between about 326° C and 350° C.