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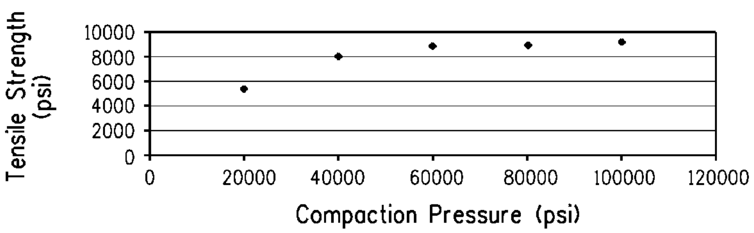


FIG. 1

(57) **Abstract**: Disclosed herein is a method for making polyimide articles that are suitable for high temperature applications. The articles disclosed herein are rigid, oxidatively stable, wear-resistant, and permeable to heated moisture and gases, and comprise co-polymer based polyimide, and at least one additive or filler, and are made using 20,000 to 50,000 psi of compression pressure.

TITLE OF THE INVENTION

CO-POLYMER BASED POLYIMIDE ARTICLES AND THEIR USES IN HIGH TEMPERATURE APPLICATIONS

FIELD OF THE INVENTION

Plastic materials have broad industrial applications, including some high temperature applications. Polyimides can be used for some higher temperature applications, but may also need to possess certain other physical properties. Disclosed herein are copolymer-based polyimide articles that are suitable for use in high temperature applications, and which also have increased permeability, durability, oxidative stability, desirable wear life and resistance to defect upon thermal exposure.

BACKGROUND OF THE INVENTION

High temperature operating conditions and industrial manufacturing require the use of materials that are tolerant of the conditions. Presently, as in the past, metal, ceramic, graphite, asbestos and other materials have been used for high temperature applications. Plastics have been useful in replacing some of these materials for high temperature applications. However, some applications also require materials that have additional properties, such as, for example, wear-resistance, chemical resistance, low-friction, decreased wear, and other properties that afford compatibility for its application.

Some applications require suitable materials that can tolerate temperatures well above 400 degrees C. For example, glass manufacturing operations are carried out at about 1400°C to 1600° C. Other systems, such as internal combustion engines require the use of materials that can sustain high temperatures, and which do not fail or wear quickly due to these high temperatures.

Materials that are used to make articles or mechanical parts that are suitable for high temperatures can be made. However, as the cross-section of the mechanical part increases, the surface area of the part is less accessible to the trapped heated moisture and gas, constraining their release. In such cases, the mechanical part is vulnerable to defects, such as blistering, due to thermal exposure of rapid thermal cycling. A progressive reduction in a part's mechanical properties can also occur with repeated cycles of moisture exposure and thermal exposure, evidenced by a reduction in measured glass transition temperature (tg) of plastics, sometimes referred to as "wet Tg knockdown".

Graphite has been used in high temperature applications, but is brittle and therefore lacks durability, cannot sustain the load applied in some applications, and lacks the wear life desired by for many applications.

Other materials made from plastics have been used, such as thermoset materials. However, many of these materials are not suitable for high temperature applications, lack strength, durability and the desired mechanical properties, leading to faster degradation over graphite.

Some polyimide materials have also been used in but may have limitations due to the temperature ranges in the particular application, or due to the inability of the polyimide part having a significant or higher cross-section relative to the surface area of the part to release heated moisture and gases upon thermal exposure, rendering it unsuitable for higher temperature applications.

The object of the present invention is to provide a method for making an article prepared from a polyimide composition wherein the article is suitable for high temperature applications, having rigidity, oxidative stability, permeability to heated moisture and gases to avoid defects caused by rapid thermal cycling, or thermal exposure.

Furthermore, the polyimide parts made by the method of the present invention are not susceptible to the build up of degraded oil residue, as is the case with graphite-based materials used in the same or similar applications.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 is a graphical representation of the tensile strength vs. compaction pressure for an article comprising copolymer-based polyimide made according the present disclosure.

Fig. 2 is a graphical representation of elongation vs. compaction pressure for an article comprising copolymer-based polyimide made according the present disclosure.

SUMMARY OF THE INVENTION

Disclosed herein is a method of making an article suitable for use in high temperature systems, said systems consisting of instrumentation and equipment, said article comprising a co-polymer based polyimide composition, wherein said composition comprises

a) an aromatic tetracarboxylic dianhydride component; and
b) a diamine component further comprising;
  (i) greater than 60 mole % to about 85 mole % p-phenylene diamine, and
  (ii) 15 mole % to less than 40 mole % m-phenylene diamine;

wherein a) and b) are present in a ratio of 1:1; and

said method comprising:

forming a part of pre-determined shape using compression; wherein the amount of pressure used in compression is from about 20,000 psi to about 50,000 psi to achieve a porous article having permeability to moisture, and resistance to defect caused by thermal exposure.

Also disclosed herein is an article suitable for use in high temperature systems, said systems consisting of instrumentation and equipment, said article comprising a co-polymer based polyimide composition, wherein said composition comprises

a) an aromatic tetracarboxylic dianhydride component; and

b) a diamine component further comprising;

i) greater than 60 mole % to about 85 mole % p-phenylene diamine, and

ii) 15 mole % to less than 40 mole % m-phenylene diamine;

wherein a) and b) are present in a ratio of 1:1; and

said article being porous and having permeability to moisture, and resistance to defect caused by thermal exposure.

DETAILED DESCRIPTION OF THE INVENTION

Polyimide materials readily absorb atmospheric moisture. Depending on the environment, the equilibrium point may be greater than 1% by weight. As a polyimide material is heated, this moisture will evolve. However, if the material is heated at a faster rate than this moisture can escape, blistering may occur.

The present invention provides a method for making an article suitable for use in high temperature systems, said systems consisting of instrumentation and equipment. The article made according the method of the present invention is an article wherein such article is durable, wear resistant over time in high temperature applications, rigid, oxidatively stable, and resistant to defect caused by rapid thermal cycling.

In the present method, the article comprises a co-polymer based polyimide composition, wherein said composition comprises

a) an aromatic tetracarboxylic dianhydride component; and

b) a diamine component further comprising;

   i) greater than 60 mole % to about 85 mole % p-phenylene diamine, and

   ii) 15 mole % to less than 40 mole % m-phenylene diamine;

wherein a) and b) are present in a ratio of 1:1; and

said method comprising:

forming a part of pre-determined shape using compression; wherein the amount of pressure used in compression is from about 20,000 psi to about 50,000 psi to achieve a porous article having permeability to moisture, and resistance to defect caused by thermal exposure.

In one embodiment of the present invention the compression pressure may be pre-determined to make an article having a certain desired density.

In one embodiment of the method in the present invention, the article may have a higher cross-section relative to the surface area of the article, and said article and is capable of releasing moisture and gas present in the cross-section of the article through the surface area of the article.

In yet another embodiment of the method disclosed herein, the polyimide composition may comprise at least one filler. The fillers used in the present invention are carbonaceous filler selected from the group consisting of natural graphite, synthetic graphite and carbon fiber; fluoropolymer, including but not limited to polytetrafluoroethylene, and inorganic fillers selected from the group consisting of kaolinite, sepiolite and mixtures thereof.

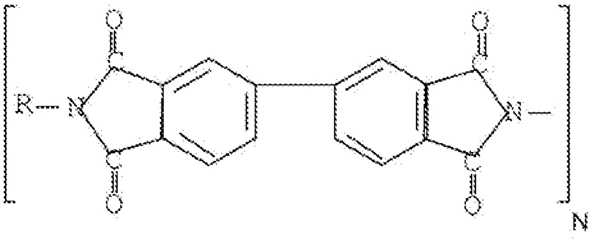
The present invention is useful in various high temperature systems, said systems consisting of instrumentation and equipment. The articles made as disclosed herein can be used to replace conventional materials used in high temperatures. For example, the articles made as disclosed herein can be used to replace mechanical elements, parts that are mainly composed of graphite, metal, ceramic, or asbestos.

Uses of the articles of the present invention are as parts in a convection oven, scientific instrumentation, such as to isolate defracting chambers, in automotive systems, including as an emission system part, internal combustion engine parts, bushing, bearing, washer, seal ring, wear pad and slide block. Additional uses of the parts disclosed herein are selected from the group consisting of a recycle system; a clutch system; a pump; a turbocharger; a thrust reverser, nacelle, a flaps system; an injection molding machine; conveyor; and tenter frame.

The present invention provides a method for making formed parts from a polyimide composition, wherein the part has improved oxidative stability and excellent tensile properties. Such formed parts are useful in high temperature applications, or applications operating at or above about 400°C. Other uses of the articles made by the method of the present invention include scientific instrumentation, convection ovens, heated conveyors, automotive applications and aerospace engines. Parts and other articles prepared using the method of the present invention are also useful in automotive engines; other vehicular subsystems such as exhaust gas recycle systems and clutch systems; pumps; non-aircraft jet engines; turbochargers; materials processing equipment such as injection molding machines; material handling equipment such as conveyors, belt presses and tenter frames; and films, seals, washers, bearings, bushings, gaskets, wear pads, seal rings, slide blocks and push pins and other applications where low wear is desirable. In some applications, a part or other article prepared according to the method disclosed herein is in contact with metal at least part of the time when the apparatus in which it resides is assembled and in normal use.

By the term “rigid polyimide” is meant is that there are no flexible linkages in the polyimide unit.

The aromatic tetracarboxylic dianhydride components used to make the copolymer polyimide of the present invention include pyromellitic dianhydride (PMDA), 3,3'4,4' -biphenyltetracarboxylic dianhydride (BPDA), and any other rigid aromatic dianhydride. Best results occur when BPDA is used as the dianhydride component. For a preferred embodiment of the present invention, the solution imidization process is used to provide a rigid, aromatic polyimide composition having the recurring unit



where R is greater than 60 to 85 mole % PPD units and 15 to less than 40 mole % MPD units. Polyimide compositions having 70% PPD and 30% MPD are preferred.

In the preparation of the present polyimide compositions, the solution imidization process is utilized according to the following. The diamines (PPD and MPD) are generally first dissolved in a solvent to form the diamine component. In general, after dissolving the diamine component in the required concentration of the solvent, the dianhydride is added to the reaction solution in substantially equimolar quantities to form a polyamide acid (PAA) polymer solution. A slight molar excess of either the dianhydride or diamine component is possible. A molar excess of 0.5 to 1.0% of the diamine component has been found to provide best results. As a general rule, better tensile properties result from closer to equimolar stoichiometry but this must be balanced against the higher viscosity that occurs as the equimolar point is approached as would be known by one of ordinary skill in the art.

The resulting PAA polymer solution is transferred over a period of time to a heated solution of the solvent. The transferred PAA polymer solution is continuously heated and agitated to complete the reaction of soluble PAA to a slurry of insoluble polyimide.

The resulting polyimide slurry is washed with solvent and dried at 100 to 230°C, preferably 140 to 190°C, more preferably 180°C, to convert the polyimide slurry to a polyimide resin in the form of a powder having a high surface area. The optimum temperature of 180°C results in greater process efficiency and better physical properties. Depending on the particle size resulting from the precipitation of polyamide acid from the reaction solution, the particles of polyimide can be further modified for example, by suitable grinding techniques, to provide a desirable particle size for handling and subsequent molding.

The solvents useful in the solution polymerization process for synthesizing the PAA polymer solution are the organic solvents whose functional groups will not react with either of the reactants (the BPDA or the diamines) to any appreciable extent. The solvent exhibits a pH of about 8 to 10, which can be measured by mixing the solvent with a small amount of water and then measuring with pH paper or probe. Such solvents include, for example, pyridine and ß-picoline. Of the solvents disclosed in Gall and U.S. Patent No. 3,179,614 to Edwards, pyridine (KB = 1.4 x 10-9) is a preferred solvent for these reactants in the polymerization reaction as well as functioning as the catalyst. For a dianhydride and a diamine to react to form a PAA polymer solution, a basic catalyst is needed. Since pyridine is a basic compound, it functions herein as both a catalyst and a solvent.

The quantity of solvent is important in obtaining a product having a high surface area. In particular, the solvent should be present in a quantity such that the concentration of the PAA polymer solution is about 1 to 15% by weight solids, preferably from about 8 to 12% by weight solids.

The surface area for a polyimide resin resulting from the polyimide composition of this invention should be at least 20 m2/g. It is preferable that the surface area be at least 75 m2/g to achieve acceptable physical properties and for ease of processability.

In the preparation of the PAA, it is essential that the molecular weight be such that the inherent viscosity (IV) of the PAA polymer solution is at least 0.2 dl/g, preferably 0.5 to 2.0 dl/g. The method for measuring and calculating IV is described below.

The polyimide composition often comprises at least one filler or one type of filler. The filler in the polyimide composition of the present invention filler may include clays, such as kaolinite or sepiolite; fluoropolymer or copolymer, such as polytetrafluoroethylene; molybdenum disulfide; and/or carbonaceous fillers such as graphite, carbon fiber. The fillers can be used to improve wear and frictional characteristics while retaining the excellent tensile and oxidative stability of the polyimide composition and parts made therefrom.

Graphite as suitable for use herein can be either naturally occurring graphite or synthetic graphite. Natural graphite generally has a wide range of impurity concentrations, while synthetically produced graphite is commercially available having low concentrations of reactive impurities. Graphite containing an unacceptably high concentration of impurities can be purified by any of a variety of known treatments including, for example, chemical treatment with a mineral acid. Treatment of impure graphite with sulfuric, nitric or hydrochloric acid, for example, at elevated or reflux temperatures can be used to reduce impurities to a desired level.

A sepiolite filler, a kaolin filler, or a mixture thereof is also suitable for use herein. A sepiolite filler suitable for use herein includes sepiolite itself

[$Mg_4Si_6O_{15}(OH)_2 \cdot 6(H_2O)$], which is a hydrated magnesium silicate filler that exhibits a high aspect ratio due to its fibrous structure. Unique among the silicates, sepiolite is composed of long lath-like crystallites in which the silica chains run parallel to the axis of the fiber. The material has been shown to consist of two forms, an α and a β form. The α form is known to be long bundles of fibers and the form is present as amorphous aggregates.

A sepiolite filler suitable for use herein also includes attapulgite (also known as palygorskite), which is almost structurally and chemically identical to sepiolite except that attapulgite has a slightly smaller unit cell.

A sepiolite filler suitable for use herein also includes clays that are layered fibrous materials in which each layer is made up of two sheets of tetrahedral silica units bonded to a central sheet of octahedral units containing magnesium ions [see, *e.g.*, Figures 1 and 2 in L. Bokobza *et al*, *Polymer International*, 53, 1060-1065 (2004)]. The fibers stick together to form fiber bundles, which in turn can form agglomerates. These agglomerates can be broken apart by industrial processes such as micronization or chemical modification (see, *e.g.*, European Patent 170,299 to Tolsa S.A.).

In one embodiment, a sepiolite filler suitable for use herein includes a rheological grade sepiolite clay, such as that which is described in EP-A-454,222 and/or EP-A-170,299 and marketed under the Pangel® trademark by Tolsa S.A., Madrid, Spain. The term "rheological grade" in this context refers to a sepiolite clay typically having an average surface area greater than 120 m^2/g [as measured in N_2 by the Brunauer/Emmett/Teller method (as described in Brunauer *et al*, "Adsorption of Gases in Multimolecular Layers", *Journal of the American Chemical Society*, 60: 309-19, 1938)], and typically having average fiber dimensions of about 200 to 2000 nm long, 10-30 nm wide, and 5-10 nm thick. Rheological grade sepiolite is obtained from natural sepiolite by means of micronization processes that substantially prevent breakage of the sepiolite fibers, such that the sepiolite disperses easily in water and other polar liquids, and has an external surface with a high degree of irregularity, a high specific surface, greater than 300 m^2/g and a high density of active centers for adsorption, that provide it a very high water retaining capacity upon being capable of forming, with relative ease, hydrogen bridges with the active centers. The microfibrous nature of the rheological grade sepiolite particles makes sepiolite a material with high porosity and low apparent density.

Additionally, rheological grade sepiolite has a very low cationic exchange capacity (10-20 meq/100 g) and the interaction with electrolytes is very weak, which in turn causes rheological grade sepiolite to not be practically affected by the presence of salts in the medium in which it is found, and therefore, it remains stable in a broad pH range. The above-mentioned qualities of rheological grade sepiolite can also be found in rheological grade attapulgite, which typically has a particle size smaller than 40 microns, such as the range of ATTAGEL® clays (for example ATTAGEL 40 and ATTAGEL 50) manufactured and marketed by Engelhard Corporation, United States; and the MIN-U-GEL range of products from Floridin Company.

A kaolin filler suitable for use herein includes kaolinite itself, which is a sheet-type silicate whose molecules are arranged in two sheets or plates, one of silica and one of alumina. Kaolinite is a clay mineral with the chemical composition $Al_2Si_2O_5(OH)_4$. It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedral sheet of alumina octahedra. Rocks that are rich in kaolinite are known as *china clay* or *kaolin*. In contrast, smectites such as montmorillonite clay minerals are arranged in two silica sheets and one alumina sheet. The molecules of the smectites are less firmly linked together than those of the kaolinite group and are thus further apart. Maintaining the phase stability of crystal structure of the sheet silicates is desirable, as is maintaining the thermal stability of the structural water of the sheet silicates at higher temperatures, such as up to about 450°C [as shown, for example, by thermogravimetric analysis (TGA)]. Loss of structural water during processing of a polyimide composition can result in harm to polyimide integrity, and possibly change the crystal structure of the sheet silicate, giving a harder, more abrasive compound. Examples of sheet silicates that are not stable enough to be included in the compositions described herein are montmorillonite, vermiculite, and pyrophyllite. Kaolin fillers suitable for use herein are discussed further in Murray, *Applied Clay Science* 17(2000) 207-221.

Sepiolite fillers and kaolin fillers that are suitable for use herein are discussed further in Murray, *Applied Clay Science* 17(2000) 207-221.

Use of graphite, sepiolite and/or kaolin as filler, in the embodiments of the present invention are typically incorporated into the heated solvent prior to transfer of the PAA polymer solution (or other solution for other types of monomers), so that the resulting polyimide is precipitated in the presence of the components (b) and (c), which thereby become incorporated into the composition.

Additives suitable for optional use in a composition hereof may include, without limitation, one or more of the following: pigments; antioxidants; materials to impart a lowered coefficient of thermal expansion, *e.g.* carbon fibers; materials to impart high strength properties *e.g.* glass fibers, ceramic fibers, boron fibers, glass beads, whiskers, graphite whiskers or diamond powders; materials to impart heat dissipation or heat resistance properties, *e.g.* aramid fibers, metal fibers, ceramic fibers, whiskers, silica, silicon carbide, silicon oxide, alumina, magnesium powder or titanium powder; materials to impart corona resistance, *e.g.* natural mica, synthetic mica or alumina; materials to impart electric conductivity, *e.g.* carbon black, silver powder, copper powder, aluminum powder or nickel powder; materials to further reduce wear or coefficient of friction, *e.g.* boron nitride or poly(tetrafluoroethylene) homopolymer and copolymers. Fillers may be added as dry powders to the final resin prior to parts fabrication.

Any one or combination of additives and/or fillers can be present in quantities ranging from 0.1 to 80 wt.%. The particular filler or fillers selected, as well as the quantities used, will, of course, depend on the effect desired in the final composition, as will be evident to those skilled in the art.

These additives or fillers are typically, but not always incorporated into the heated solvent prior to transfer of the PAA polymer solution so that the polyimide is precipitated in the presence of the filler which is thereby incorporated. In some cases, the filler(s) or additive(s), or both, is dry blended with the polyimide particulate. The form of the fillers will depend on the function of the filler in the final products. For example, the fillers can be in particulate or fibrous form.

As stated previously, the polyimide compositions of the present invention are oxidatively stable. To test oxidative stability, tensile bars are formed as described below and then subjected to extreme temperatures for a fixed, lengthy period of time. The tensile bars are weighed both before and after testing and percent weight loss is calculated. The rigid, aromatic polyimide compositions of the present invention are considered to be oxidatively stable if the percent weight loss is less than 5%, preferably less than 3%, because such a weight loss would not compromise the integrity of the tensile bar, or more specifically, parts made by the method of the present invention as disclosed herein.

The polyimide articles of the present invention are characterized not only by the excellent thermal oxidative stability alone, or any one property alone, but by the exceptional tensile properties, together with other properties that are not insignificant in high temperature applications, such as durability, wear resistance and wear life, rigidity, permeability to heated moisture and gas, and resistance to defect upon thermal exposure . Both tensile strength and elongation are particularly important properties for applications as described above. As is generally known to those of ordinary skill in the art, products having low elongation tend to be brittle which leads to cracking during machining or in load bearing applications.

The polyimide composition made as disclosed herein can be molded under elevated pressures to a wide variety of configurations. For many applications, the polyimide composition is molded at pressures of about from 50,000 to 100,000 psi (345 to 690 MPa) at ambient temperatures.

The method of making the articles for high temperature applications, including the permeability of heated moisture and gases is a direct forming method, and is carried out by introducing the polyimide composition to a mold, sintering the polyimide composition at elevated temperatures of from about 300°C to about 450°C while compressing the part using from about 20,000 psi to about 50,000 psi, preferably from about 35,000 psi to about 45,000 psi, and most preferably about 40,000 psi of pressure to form a the article or part.

The articles or parts made by compressing the polyimide composition at from about 20,000 psi to about 50,000 psi are useful in high temperature applications. More particularly, the articles of parts made by the method of the present invention are useful in glass manufacturing, and more particularly glass container manufacturing. Such articles or parts include, but are not limited to glass handling assemblies, and components thereof. These include take-out jaw assemblies and components thereof, including take-out jaw inserts, dead plates, sweep out devices, stacker bars, stacker bar pads, stacker bar bearings, and components of any of these.

Polyimide materials readily absorb atmospheric moisture. Depending on the environment, the equilibrium point may be greater than 1% by weight. As a polyimide material is heated, this moisture will evolve. However, if the material is heated at a faster rate than this moisture can escape, blistering may occur. This phenomenon can limit the use of the polyimide material in many applications. In order to overcome this limitation, we have investigated ways to increase the permeability of the polyimide material. We have demonstrated that compacting or compressing of the polyimide material at lower pressures can result in a more porous structure with significantly better resistance to blistering during thermal exposure, or during exposure to rapid thermal cycling. We have also demonstrated that this can be done without significantly affecting the mechanical properties of the material which is key to its high temperature wear performance and durability.

The co-polymer based polyimide used in the method(s) and in the article(s) of the present invention imparts certain advantages in high temperature applications such as hot glass handling applications, aircraft engines and parts, or analytical scientific instruments, over the use of traditional and commonly used polyimide materials, and carbon graphite materials (for example, free of polyimide).

The methods and uses disclosed herein provide low thermal conductivity, demonstrating approximately 50 to 100 times lower heat transfer coefficient versus articles prepared using traditional carbon graphite. Lower thermal conductivity of the articles of the present invention, and related use of the articles of the present invention, impart minimization or elimination of blisters, and micro-cracks, thereby lowering quality rejects and improving productivity.

It is also found that the method articles of the present invention provider high impact resistance at 70 to 100% higher than carbon graphite parts that are traditionally used in hot glass manufacturing applications. Reduced breakage of the articles during fabrication, handling and use extends the life of the articles, which then increases process reliability and reduces operating costs.

Oil absorption is also observed in the methods and articles of the present invention. The components made in the present invention absorb 30 times less oil than carbon graphite parts to zero oil absorption. Reduced or eliminated oil absorption affords the advantage of reduced checking in the containers handled by the articles, thus an increased yield of the containers, and reduced operating costs.

Another advantage of the method and articles of the present invention is reduced wear. Test results show three times less wear versus carbon graphite at 600 degrees F (315 degrees C) in oscillatory conditions, demonstrating 2 to 11 times longer life over glass handling carbon graphite take-out inserts. Such an advantage translates into significantly longer life of consumables to increase production efficiency.

EXAMPLES

Compaction Pressure (psi)	Tensile Strength (psi)	% Elongation	Specific Gravity	TOS	Blistering Temperature
20000	5323	0.9	1.551	3.46%	Pass at 400°C
40000	8096	1.5	1.632	3.09%	Pass at 400°C
60000	8858	1.6	1.665	2.19%	Fail at 325°C - 400°C
80000	8892	1.5	1.674	1.75%	Fail at 325°C - 400°C
100000	9204	1.6	1.683	1.68%	Fail at 325°C - 400°C

For the test data described in the above table, the polyimide composition as disclosed herein samples were fabricated into tensile bars according to ASTM E8 – “Standard Tension Test Specimen for Powdered Metal Products – Flat Un-machined Tensile Test Bar” at room temperature and at pressures ranging from 20,000 to 100,000 psi. The tensile bars were sintered at 405C with a nitrogen purge for 3 hours. Tensile strength and elongation were measured according to ASTM D638.

Specific Gravity was measured using Archimedes principle (i.e. volume determined by measuring specimen weight in water and subtracting it from its dry weight. This volume is then divided into the dry weight to determine the specific gravity.)

Thermal Oxidative Stability (TOS) was tested by first immersing tensile bars or parts of tensile bars in alcohol for 15 minutes and drying at 300F for 1 hr. Upon cooling, the specimens are weighed and then exposed to a temperature of 700F for 100 hrs at a pressure of 70 psia in air. The final weight measurement is then taken and a percent weight loss of the tensile bars was calculated according to the following formula:

$$\% \text{ Weight loss} = (\text{Initial wt.} - \text{Final wt.} / \text{Initial wt}) \times 100$$

Resistance to blistering during thermal exposure or rapid thermal cycling is tested by first immersing a tensile bar or part of a tensile bar in 95°C water for 12 days. Next, the specimen is placed in a preheated oven at the specified temperature. A passing result is obtained when no visible cracking or blistering are present in the specimen after this thermal exposure. Samples compacted at 20,000 and 40,000 psi showed no visual defects after exposures up to and including 400°C. Samples compacted at 60,000 – 100,000 psi showed defects after exposure to temperatures of 325°C and above.

It is noteworthy that the specimens compacted at 40,000 psi retained 88% of the Tensile Strength and 94% of the Elongation of specimens compacted at 100,000 psi while exhibiting positive blistering resistance performance at 400°C vs. only 325°C for the specimens compacted at higher pressures.

It should be noted that other methods can be employed to obtain low-density or increased pore density parts, such as the addition of scarificial fillers that degrade or ablate or crush upon a thermal, chemical or mechanical processing step, resulting in a network of pores or pathways for moisture to egress. However, the method described herein is economic as additional fillers and processing steps are not required, while achieving a part with suitable mechanical integrity for high temperature application.

EXAMPLE 2: Comparative Analyses

PROPERTY COMPARISONS TRADITIONAL POLYIMIDE AND GRAPHITE VS CO-POLYMER BASED POLYIMIDE

Property	**Units**	**Traditional polyimide**	**Traditional Carbon graphite**	**Co-polymer based Polyimide of the present in invention**
Izod impact (Notched heat aged at 315°C Using ASTM D-256	J/m	28	17	**33**
Oil Absorption	% wt change	0.12	5.74	**0.19**
Wear (oscillating at 315°C/25 hr)	% wt loss	1.53	3.1	**0.96**
Thermal Conductivity	W/mK	1	80	**2**

In "Example 2: Comparative Analyses", the results in the column labeled "Traditional Polyimide" were obtained using a sample of 60 weight percent conventional polyimide and 40 weight percent graphite. "Traditional Carbon-graphite" results were obtained using graphite, free of polyimide.

"Co-polymer based Polyimide of the present invention" results were obtained using a sample of 50 weight percent polyimide composition as disclosed herein and 50 weight percent graphite.

CLAIMS

What is claimed is:

1. A method of making an article suitable for use in high temperature systems, said systems consisting of instrumentation and equipment, said article comprising a co-polymer based polyimide composition, wherein said composition comprises

   a) an aromatic tetracarboxylic dianhydride component; and

   b) a diamine component further comprising;

      (i) greater than 60 mole % to about 85 mole % p-phenylene diamine, and

      (ii) 15 mole % to less than 40 mole % m-phenylene diamine;

   wherein a) and b) are present in a ratio of 1:1; and

said method comprising:

forming a part of pre-determined shape using compression; wherein the amount of pressure used in compression is from about 20,000 psi to about 50,000 psi to achieve a porous article having permeability to moisture, and resistance to defect caused by thermal exposure.

2. The method of claim 1 wherein said compression pressure is from about 35,000 psi to about 45,000 psi.

3. The method of claim 1 wherein said compression pressure is about 40,000 psi.

4. The method of claim 1 wherein said article has a higher cross-section area relative to the surface area of the article, and said article and is

capable of releasing moisture and gas present in the cross-section area of the article through the surface area of the article.

5. A method of claim 1 wherein said polyimide composition comprises at least one filler or additive.

6. The method of claim 5 wherein said filler is carbonaceous filler, said carbonaceous filler being selected from the group consisting of natural graphite, synthetic graphite and carbon fiber.

7. The method of claim 6 wherein said filler is fluoropolymer and said fluoropolymer is selected from the group consisting of polytetrafluoroethylene.

8. The method of claim 5 wherein said filler is selected from the group consisting of kaolinite, sepiolite and mixtures thereof.

9. An article made by the method of claim 1.

10. The article according to claim 9 wherein said article is suitable for use in an analytical scientific instrument to isolate defracting chambers.

11. The article according to claim 9 wherein said article is suitable for use in a convection ovens or heated conveyors.

12. The article according to claim 9 wherein said article is suitable for use in an automotive engine or automotive subsystem.

13. The article according to claim 12 wherein said automotive subsystem is selected from the group consisting of exhaust gas recycle system, clutch system, pump, and turbocharger.

14. The article according to claim 12 wherein said article is a seal, washer, bearing, bushing, gasket, and seal ring.

15. An article of manufacture suitable for use in high temperature systems, said systems consisting of instrumentation and equipment, said article comprising a co-polymer based polyimide composition,
wherein said composition comprises

a) an aromatic tetracarboxylic dianhydride component; and
b) a diamine component further comprising;
    i) greater than 60 mole % to about 85 mole % p-phenylene diamine, and
    ii) 15 mole % to less than 40 mole % m-phenylene diamine;

wherein a) and b) are present in a ratio of 1:1; and
said article being porous and having permeability to moisture, and resistance to defect caused by thermal exposure.

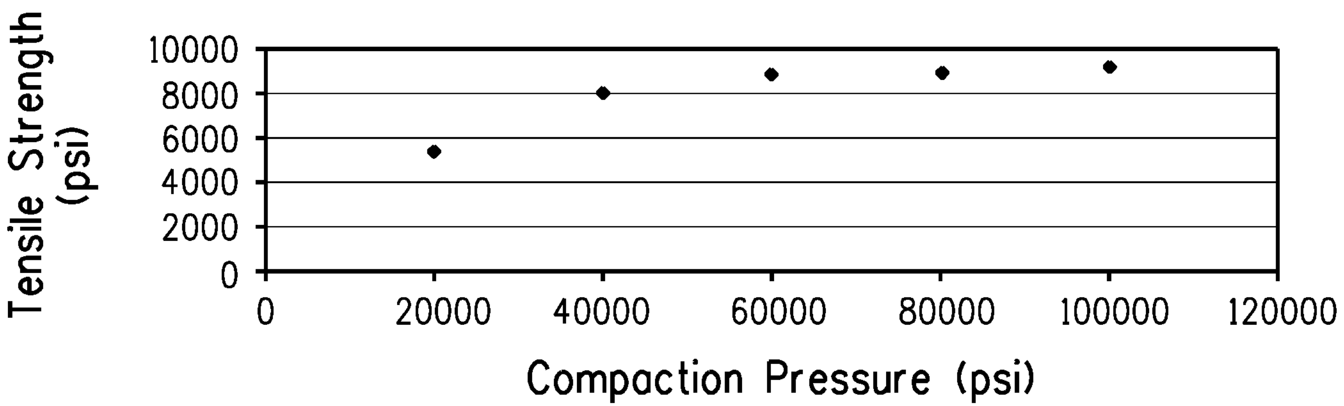

Tensile Strength (psi)
10000
8000
6000
4000
2000
0
0
20000
40000
60000
80000
100000
120000
Compaction Pressure (psi)

FIG. 1

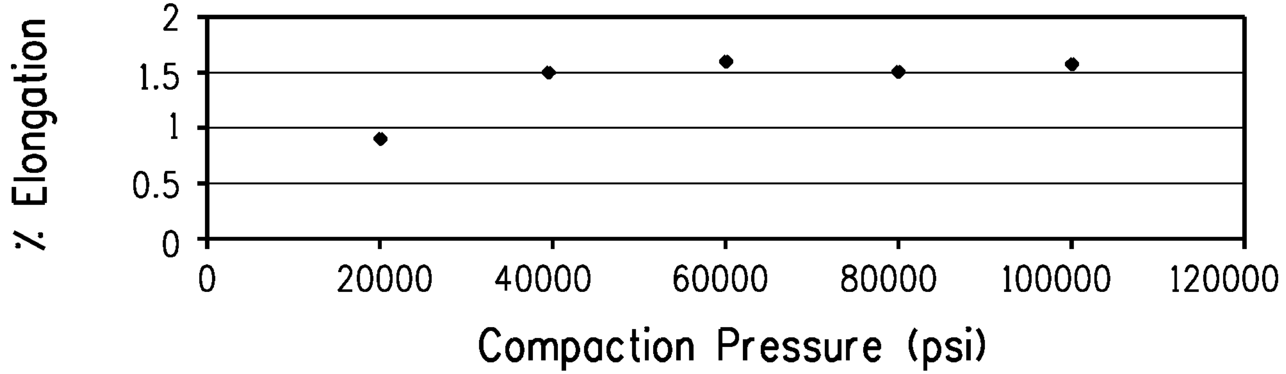

% Elongation
2
1.5
1
0.5
0
0
20000
40000
60000
80000
100000
120000
Compaction Pressure (psi)

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/027487

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G73/10 C08J9/00 C08L79/08 C08K3/00 C08K3/04
B29C43/00 B29C43/02 F24C15/00 F02B37/00 C09J9/00
F02M25/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08G C08J B29D C08L C08K B29C F24C F02B C09J F02M

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/079365 A1 (DU PONT [US]; GANNETT THOMAS P [US]) 3 July 2008 (2008-07-03)	1-15
Y	examples 1,2,12 page 11, line 21 - page 12, line 7 -----	1-15
X	US 5 900 197 A (MATSUI AKIRA [JP] ET AL) 4 May 1999 (1999-05-04)	1-15
Y	column 6, lines 1-15, 49-53 column 15, lines 12-30 -----	1-15
X	DATABASE WPI Week 200033 Thomson Scientific, London, GB; AN 2000-382136 XP002586425 -& JP 2000 129001 A (UBE IND LTD) 9 May 2000 (2000-05-09)	1-15
Y	* abstract ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 23 July 2010	Date of mailing of the international search report 03/08/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Barrère, Matthieu

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/027487

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 2002/037995 A1 (TSUMIYAMA TATSUO [JP]) 28 March 2002 (2002-03-28) example 1	1-15
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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