

TITLE**RESIN COMPOSITIONS WITH A LOW COEFFICIENT OF THERMAL
EXPANSION AND ARTICLES THEREFROM**

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This application claims the benefit of U.S. Application No. 60/685,370,
filed May 27, 2005.

FIELD OF THE INVENTION

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This invention generally relates to resin compositions having a reduced coefficient of thermal expansion. Specifically, this invention relates to resin compositions wherein the lower coefficient of thermal expansion is achieved by addition and mixing of at least one filler material to the resin composition in question. This invention further relates to articles made from such resin compositions having a reduced coefficient of thermal expansion. This
15 invention also relates to a method for making such articles.

BACKGROUND OF THE INVENTION

A seal ring is used for sealing lubricant oil fluid in automatic transmission assembly
20 (AT) where rotating parts in the equipment are involved, for example, in a car engine. Soft aluminum alloys are used for the rotary shaft and the housing thereby making the AT lightweight.

The seal ring is made from a polymeric resin material, metals, etc. For example, cast iron has been widely used for making the seal ring because cast iron shows very good sliding
25 characteristic when AT is fully lubricated by the ATF (automatic transmission fluid). However, the cast iron seal ring can wear out the rotary shaft and the housing assembly much faster as it has a hardness higher than the lightweight aluminum alloy used for AT. This problem is further aggravated when the AT is running with a reduced level of ATF. Further, cast iron is a stiff material. This can be problematic during installation of the seal ring.
30 Moreover, the efficiency of the seal is compromised when the ATF oil pressure is low.

For facilitating installation or attachment of the seal ring to the AT, a seal ring is subjected to a cut called the gap joint. When the temperature of the AT and the ATF rise, thermal expansion of the seal ring closes this gap or cut. However, because of the gap joint, it is possible that the seal performance is inconsistent.

Polytetrafluoroethylene (PTFE) is also used as a seal ring material. Because PTFE is soft, it can cause a drag during installation and subsequently, a fracture in the ring. Also, because PTFE resin has especially a relatively large thermal expansion coefficient, the change in amount of ATF leakage is also large. Further, as the temperature of the AT and ATF increase the seal expands causing compression resulting into a creep modification. Although the seal ring circumference may be lengthened by a corresponding amount to offset the creep modification, the external size of the seal ring becomes larger than the inner diameter size of the housing and the fitting of the ring does not remain tight.

Moreover, when the hardness of the material is low, a solid foreign substance embedded into the seal ring can wear out the mating material.

Polyimide resin has also been used as a seal ring material. Its physical mechanical properties are especially suitable to form the gap joint. However, the rate of ATF leakage changes with thermal expansion, although the problem may not be as serious as PTFE. Thus, seal performance suffers. Graphite or other inorganic compounds have been added to reduce the coefficient of thermal expansion, which helps the seal performance. However, defects during gap joint formation and a lowering of flexural strain as a result of the additives can undermine the seal performance.

The present invention addresses these problems. The inventors of the present invention have discovered an optimum composition of the seal ring material such that the flexural strain does not drop below the critical limit required for adequate seal performance and simultaneously, the coefficient of thermal expansion is also lowered such that the seal performance is improved over conventional seal rings over a broad temperature range. *Inter alia*, the present invention discloses an additive graphite material with a specific surface area range, a specific particle size and its percent by weight in the seal ring material that provides the desired seal performance from the seal rings made by this material.

SUMMARY OF THE INVENTION

In one embodiment, there is provided a composition comprising:
(a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide,

copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole copolymers of fluoropolymer and compatible blends thereof;

(b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material have a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and

(c) optionally, a fiber selected from the group consisting of aramid fiber, glass, fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%.

In a first aspect, there is provided a composition comprising:

(a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole copolymers of fluoropolymer and compatible blends thereof;

(b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and

(c) optionally, a fiber selected from the group consisting of aramid fiber, glass fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%, wherein said polymer is a polyimide, wherein said polyimide is prepared by a condensation polymerization reaction of an aromatic tetracarboxylic dianhydride or derivative thereof, and a diamine or derivative thereof, wherein said aromatic tetracarboxylic dianhydride is selected from the group

consisting of pyromellitic dianhydride, biphenyl tetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, and combinations thereof; and wherein said diamine is selected from the group consisting of 4,4'-diamino diphenyl ether, 3,4'-diamino diphenyl ether, p-phenylene diamine, m-phenylene diamine, and combinations thereof.

OR

wherein said polyimide is made from pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA);

OR

wherein said polyimide is a copolymer of polyimide derived from 3,3',4,4'-biphenyl tetracarboxylic dianhydride with p-phenylene diamine and/or m-phenylene diamine.

In one embodiment, there is provided articles comprising a matrix resin material, said matrix resin material having a composition comprising:

- (a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole copolymers of fluoropolymer and compatible blends thereof;
- (b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and
- (c) optionally, a fiber selected from the group consisting of aramid fiber, glass, fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%.

Finally, this invention relates to a process for making an article, said article comprising a matrix resin material, said matrix resin material having a composition comprising:

(a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole, copolymers of fluoropolymer and compatible blends thereof;

(b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and

(c) optionally, a fiber selected from the group consisting of aramid fiber, glass, fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%;

wherein said article is made by a process selected from the group consisting of powder compression, compression molding, extrusion molding, injection molding and reaction injection molding.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more fully understood from the following detailed description, taken in connection with the accompanying drawings, in which:

FIG. 1 depicts the evaluation equipment for measuring the relationship between the amount of oil (automatic transmission fluid) leak and the temperature of the seal ring.

FIG. 2 depicts the relationship between coefficient of thermal expansion and the percent weight of graphite additive to polyimide.

FIG. 3 depicts the relationship between the flexural strain of polyimide and percent weight of graphite additive to the polyimide.

FIG. 4 depicts the rate in ml/min of automatic transmission fluid leak as a function of temperature.

While the present invention will be described in connection with a preferred embodiment thereof, it will be understood that it is not intended to limit the invention to that embodiment. On the contrary, it is intended to cover all alternatives, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

This invention generally relates to resin compositions having a reduced coefficient of thermal expansion. Specifically, this invention relates to resin compositions wherein the lower coefficient of thermal expansion is achieved by addition and mixing of at least one filler material to the resin composition in question. This invention also relates to a process for making such resin compositions. This invention further relates to articles made from such resin compositions having a reduced coefficient of thermal expansion.

Resin Composition

Generally, the resin composition comprises high-temperature polymeric materials such as engineering polymers. Polymeric materials useful for the present invention include homopolymers and copolymers of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole and fluoropolymer.

Preferred resin compositions are polyimides prepared by condensation polymerization reaction of diamine and acid. Examples of acid anhydride include pyromellitic dianhydride, biphenyl tetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, etc. Examples of diamine include 4, 4'-diamino diphenyl ether, 3, 4'-diamino diphenyl ether, p-phenylene diamine, m-phenylene diamine, etc.

Another preferred resin composition is KaptonTM, a polyimide (PI) made from pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA). Further preferred resin composition is a polyimide copolymer derived from 2,3,3',4'-biphenyl tetracarboxylic dianhydride with p-phenylene diamine and/or m-phenylene diamine.

A further preferred resin composition is an aromatic polyimide composition prepared substantially in accordance with the method described in U. S. Patent 3,249,588, which is incorporated by reference herein.

The resin compositions used in the present invention generally have outstanding
5 mechanical properties, improved thermal and chemical resistance and stability and even good sliding characteristics.

Filler Material

The filler material is mixed with the resin composition during resin formation and/or
10 during processing of the resin composition to prepare the article of use.

Preferred filler material for this invention is graphite. It is preferred for the present invention to use graphite consisting of non-spherical, rounded particles. These particles may be best described as having a potato-like shape or a globular shape. U.S. Patent No. 2004/0053050 to Guerfi et al. discloses techniques for preparing graphite particles for use in
15 lithium-ion batteries, such graphite being described as "potato-like" in shape. Mathematical methods for describing particle shape are also described. U.S. Patent No. 5,169,508 to Suzuki et al. contains the term "globular" to describe a graphite particle shape, such graphite being used in electrode applications. JP 05331314 to Tanaka et al. discloses use of spherical graphite in a "Heat-Resistant Resin Sliding Material." A description used for the graphite
20 particles is "close to perfect sphere" with a smooth surface, very hard, and of uniform size distribution. A reference in the open literature (M.C. Powers, Journal of Sedimentary Petrology, vol. 23, no. 2, (1953) pp. 117-119) describes a qualitative roundness scale for particle characterization. Using that scale, the graphite particles of this invention are of intermediate sphericity, and in the range of "sub-angular" to "rounded" The mid-range is
25 termed "sub-rounded."

A preferred weight of graphite in the article is in the range of from about 35% to about 70% of the total weight of the article.

A preferred specific surface area of the graphite material is about $10 \text{ m}^2/\text{g}$ or less. A further preferred specific surface area of the graphite material is in the range of from about
30 $1 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$. An even further preferred specific surface area of the graphite material is in the range of from about $2 \text{ m}^2/\text{g}$ to about $7 \text{ m}^2/\text{g}$. A further preferred specific surface area of the graphite material is about $5 \text{ m}^2/\text{g}$.

A preferred particle size of the filler material graphite is about 100 microns or less. A more preferred particle size of the filler material graphite is selected from about 75 microns or less, 50 microns or less, and 30 microns or less.

It is also further preferred that said graphite filler material is non-spherical and rounded in shape. The graphite filler material has a sphericity of less than about 1. The bulk density of said graphite is at least about 0.20 g/cm³.

Fibers in the Matrix

In addition to the filler material described above, an article prepared from said resin composition material may comprise fibers in its matrix for reinforcement or other purposes. Fibers used for this application are selected from aramid fibers, glass fibers, carbon fibers and mixtures thereof. The percent weight of said fibers in such an article is in the range of from about 0% to about 10% of the total weight of the article.

Method of Making Articles

Articles with lower coefficient of thermal expansion can be prepared by the method of this invention. Generally, the graphite filler material as described above is mixed with a resin composition during a conventional process of making such articles known to one skilled in the pertinent art, for example powder compression, compression molding, extrusion molding, injection molding, reaction injection molding, etc. Fibers such as aramid, glass and/or carbon may be added during processing of the article or during resin formation. Sometimes, the resin formation and the step of making the article can be one and the same.

Articles of Use

Articles with low coefficient of thermal expansion can be made by the composition and method disclosed in this invention. Two exemplary embodiments of the present invention, i.e., articles of use, are described below. Other articles, wherein a low coefficient of thermal expansion is desired, can be made using the composition and method of this invention.

Seal Ring or Gasket

In one embodiment, an article of use is a seal ring or a gasket. Such a seal ring can be used in equipment in static environment where generally there are no moving parts. Such a ring can also be used in equipment where moving parts or movement is involved, for

example, reciprocating movement or rotary movement. Such rings can also be used for applications wherein a fluid pressure is exerted on such a ring. Pressure exerted when a liquid or a gas evolves during a process can employ such rings. Such rings can also be employed where a seal is required to avoid oil leaks under pressure, such as a transmission fluid leak in an automatic or in pump action.

Further, such rings can also be employed in situations where said ring is compressed from the outside (i.e., the force acts on the outside surface of the ring) in a radial direction toward the center of the seal ring, or in situations where the force acts on the inner surface of the ring, for example, when an equipment chamber is under suction or vacuum (negative pressure). Obviously, such rings can also be employed in situations where both a compression force on the outer surface and a suction force on the inner surface are simultaneously and/or intermittently applied. Applications of such seal rings, described in U.S. Pat. No. 5,988,649, are herein incorporated by reference.

A seal ring can be made by using the process of present invention and the materials of the present invention. A seal ring can be used, for example, in sealing off automatic transmission fluids. This particular operation occurs generally at high temperature and high pressure, coupled with a relative rotary movement between the rotation shaft and the housing over an extended period of time. Therefore, for this use, it is advantageous to have a seal ring material with outstanding sliding characteristics, thermal and chemical resistance and mechanical integrity to withstand the harsh environment of operation. Particularly, the seal ring should provide insulation such that fluid leak is completely stopped, or is negligible or is at least minimal, and constant while the operating temperature of the automatic transmission assembly fluctuates from low to high.

In recent years, metal alloys have been used in automatic transmission, for example, aluminum alloy, to make the automatic transmission assembly lightweight. The lightweight alloys can generally be physically softer. It is therefore advantageous that the seal ring not damage the soft mating materials to which the seal ring is likely to come in contact. With a higher coefficient of thermal expansion, an increase in temperature will expand the seal ring such that it may damage the lightweight alloy materials used in the automatic transmission assembly. It is an object of the present invention to provide a seal ring with a reduced coefficient of thermal expansion such that the damage to the automatic transmission assembly is minimized. Generally, a seal ring has an indentation or a cut on its circumference so that it attaches snugly to the rotation shaft. This indentation or cut is also known as a joint gap. Various forms of joints can be used, for example, bat joint, scarf joint, step joint, etc., known

to a person skilled in the pertinent art. This joint gap on the seal ring is important in preventing oil leaks (automatic transmission fluid leaks) and also for facilitating attachment of the seal ring to the rotation shaft.

In one embodiment, the joint is created by fracturing the seal ring. Fracture is accomplished by providing a physical shock (force) to a polymeric material below its glass transition temperature T_g . This is similar to the shock division method used for division processing of large terminal of the connection rod, which connects the piston and crank of an automobile engine. Generally, fracture is usable only when a material does not have a plastic modification region (i.e., below glass transition temperature, in case of a polymeric material such as polyimide) at the fracture processing conditions. Polymers that exhibit a plastic deformation at room temperature can be fractured by exposure to liquid nitrogen or other cryogenic conditions immediately followed by fracture. A method for applying fracture to form a joint in a seal ring is given in U.S. Pat. 5,988,649, which is incorporated by reference herein.

When the force exerted on the ring exceeds the maximum limit of the tensile stress of the ring material,, a brittle fracture occurs with the crack propagation from the inside surface of the ring to the outside surface of the ring. Depending upon the resin composition of the ring material and the temperature at which the ring is the pressure is exerted on the ring, the ring will have pre-determinable physical characteristics of flexural strain and coefficient of thermal expansion.

Figure 1 depicts the evaluation equipment for measuring the relationship between the amount of oil (automatic transmission fluid) leak and the temperature of the seal ring. The shaft 1 is made from aluminum (e.g. aluminum alloy for die-casting). The housing 2 is also made from aluminum (e.g. aluminum alloy for die-casting). The seal ring 3 is shown as part of the housing. The oil supply pipe 4 connects to the housing 2. The supply pipe 4 has an oil pressure gauge 5. The oil pump 6 supplies oil through the supply pipe 4 from the oil tank 7. The measuring cylinder 8 measures the amount of the oil leak through a valve 9.

When the coefficient of thermal expansion of the material of the seal ring differs greatly from that of the automatic transmission assembly (rotation shaft and the housing), a fluctuation in temperature will result into a relatively different expansion and contraction of the seal ring and the automatic transmission assembly. Consequently, automatic transmission fluid has a higher likelihood of leakage from the gap joint of the seal ring that also expands and contracts. A leakage will affect the performance of the automatic transmission. In order to maintain a minimum, and a relatively constant leakage of automatic transmission fluid, the

inventors of the present invention have found that it is important to maintain the coefficient of thermal expansion in the range of from about 15 micrometer/m-°C to about 25 micrometer/m-°C for automatic transmission assembly comprising aluminum alloys.

Coefficient of thermal expansion of a material can be lowered by adding fillers such as graphite, carbon fiber, etc. However, addition of such filler materials to reduce the coefficient of thermal expansion, also reduces the flexural strain of the material. A reduction in flexural strain of a material is not a desirable characteristic in this application, i.e., a seal ring.

Figure 2 depicts the relationship between coefficient of thermal expansion and the percent weight of graphite additive to polyimide, a seal ring material. It also shows the same relationship when the said polyimide material was reinforced with aramid fiber. With an increase in weight percent of graphite additive, the coefficient of thermal expansion is lowered. When the aramid fiber was added, the coefficient of thermal expansion was further lowered at all percent weight of the additive graphite. This is a desirable result.

Figure 3 depicts the relationship between the flexural strain of polyimide, a seal ring material, and percent weight of graphite additive to the polyimide. Relationship is shown for both a conventional graphite additive and the graphite additive of this invention. The graphite additive of this invention is described below. It can be seen from Figure 3 that the flexural strain decreases with an increase in the graphite additive content in the polyimide material. However, it is also seen that the flexural strain for the polyimide with conventional graphite additive is always lower than that for polyimide with graphite additive of this invention, at all percent weight of graphite in the polyimide.

Moreover, the rate in ml/min of automatic transmission fluid leak as a function of temperature is shown in Figure 4.

The inventors also found that a flexural strain of at least about 1.8% is required in order to carry out a suitable fracture processing when forming the joint for the fractured seal ring. If the flexural strain is less than about 1.8%, during fracture process for preparing the gap joint, the seal ring is brittle to the extent that material is chipped off at the site where fracture is desired. In addition, the fracture may not take place at the desired location on the seal ring.

The inventors of the present invention have solved the problem of maintaining the flexural strain to at least about 1.8% while reducing the coefficient of thermal expansion by addition of graphite additive with specific physical properties.

Graphite demonstrates excellent lubricating and sliding property characteristics.

A preferred weight percent of graphite of the total weight of the seal ring is in the range of from about 35% to about 70%. Furthermore, a preferred specific surface area of the graphite additive is in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$. A more preferred range is about $5 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$ or from about $2 \text{ m}^2/\text{g}$ to about $7 \text{ m}^2/\text{g}$. A most preferred specific surface area is about $5 \text{ m}^2/\text{g}$.

As described previously, if the percent weight of graphite is reduced to maintain the flexural strain above 1.8%, the coefficient of thermal expansion increases beyond 25 micrometer/ m°C resulting into undesirable leaks. On the other hand, if the graphite additive is added in the amount such that the coefficient of thermal expansion is within the desired range of from about 15 micrometer/ m°C to about 25 micrometer/ $^\circ\text{C}$, but if the specific surface area of the said graphite additive is more than about $10 \text{ m}^2/\text{g}$ then the flexural strain of the seal ring is lowered to less than about 1.8%, which is undesirable for fracture purposes.

Therefore, the inventors have discovered a range of specific surface area of the graphite additive and the range of the weight percent of the graphite additive that addresses both, the lowering of the coefficient of thermal expansion such that it falls within the range of from about 15-25 micrometer/ m°C as well as the maintenance of the flexural strain above 1.8%.

Further, it is preferred that the graphite used for the present invention have a non-spherical and rounded shape. A preferred sphericity of said graphite particles is less than 1.

It is also preferred that the average particle size of the graphite additive is less than about 100 microns.

EXPERIMENTAL

EXAMPLE 1

PMDA-ODA (pyromellitic acid dianhydride and 4,4'-oxydianiline) polyimide resin particles containing about 57% by weight of a spherical graphite additive material with an average diameter of 20 microns (manufactured by Nippon Graphite Industries, as LB-CG graphite) were prepared and molded into test pieces using a procedure substantially according to the procedure described in U.S. Pat. 4,360,626, which is incorporated by reference herein.

COMPARATIVE EXAMPLES 1-9

For the comparative examples, resin compositions and various test pieces were made by the same method as described in Example 1. However, different types of graphite additive materials were added. Table 1 shows the different types and amounts of graphite additive materials added to the resin compositions. The graphite additive materials of the comparative examples C1-3, C5, and C6 were manufactured by Nippon Graphite Industries, those of the comparative examples C4, C7, C8, and C9 were manufactured by Asbury Carbons.

The results are shown in Table 1 and selected examples are depicted graphically in Figures 2 and 3. Moreover, the rate in ml/min, of automatic transmission fluid leak as a function of temperature is shown in Figure 4.

Tablet shows the data for the examples and comparative examples

		Examples					Comparative samples								
	Unit	E1	E2	E3	E4	E5	C1	C2	C3	C4	C5	C6	C7	C8	C9
Loading % of graphite	wt %	57	57	57	57	57	flake	flake	flake	flake	spherical	flake	flake	flake	flake
Form of graphite		Natural	Natural	Natural	Natural	Natural	Natural	Natural	Synthetic	Natural	Natural	Synthetic	Synthetic	Natural	Natural
Source of graphite															
Specific surface area of graphite	m ² /g	4.5	6.5	2.5	4.5	4.5	12.2	7.5	155.3	20	4.5	155.3	15	20	20
Bulk density of graphite	g/cm ³	0.48	0.26	0.62	0.46	0.48	0.09	0.08	0.10	0.16	0.48	0.10	0.14	0.16	0.16
Average particle size of graphite	X 10e-6 m	20	12	57	20	20	5	5	7	8	20	7	8	8	8
Other fillers and its loading %		No addition	No addition	No addition	No addition	P-aramid chopped fiber 5%	No addition	No addition	No addition	No addition	No addition	No addition	No addition	No addition	No addition
Examination results															
Tensile Elongation	%	2.2	2.1	2.3	1.5	2.4	1.4	0.9	1.4	1.5	No data	No data	3.5	2.9	5.0
Flexural strain	%	3.0	2.8	2.9	2.5	3.6	1.5	1.4	1.6	1.6	3.5	1.8	2.7	2.0	4.1
Flexural strength	MPa	84	71	57	57	83	84	81	83	86	96	90	90	73	105
Coefficient of thermal expansion	X 10e-5 m/C	20	22	20	19	15	16	22	18	16	33	30	29	29	40
Coefficient of Friction		0.07	0.07	0.07	0.07	0.08	0.07	0.07	0.09	0.09	0.07	0.08	0.06	0.08	0.07
Wear of seal ring	X 10e-8 m ³ /hr	10	9	11	9	8	18	20	5	15	11	7	30	12	8
Wear of mating material	X 10e-6 m ³ /hr	3	3	4	3	3	3	3	1	10	3	1	1	5	3
Defect rate of the process for fractured seal ring		Good	Good	Good	Good	Good	Good	Good	Good	Bad	Good	Good	Good	Fair	Good
		Good	Good	Good	Good	Good	Bad	Bad	Bad	Bad	Good	Fair	Good	Good	Good
Easiness of assembling seal ring to shaft		Good	Good	Good	Good	Good	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Good
		Good	Good	Good	Good	Good	Bad	Bad	Bad	Bad	Good	Good	Good	Good	Good

Note

* Defect rate of seal ring in the fractured process

Good : Defect < 1/1000, Fair : Defect < 1/1000 - 5/1000, Bad : Defect > 5/1000

** Easiness of assembling seal ring to shaft

Good : Easy to assemble with no break, Bad : Difficult to assemble due to too brittle

TEST METHODS

Coefficient of Thermal Expansion

5

The coefficient of thermal expansion was measured using The Thermal Analyst 2000 thermal analysis equipment (DuPont Instruments). The coefficient of thermal expansion was measured in the circumferential direction for a seal ring.

10

The test samples had a width of 3mm, a height of 3mm, and a length of 5mm and the measurement temperature range was from 23°C through 150°C. The linear coefficient of thermal expansion between the said temperatures was measured.

Flexural Strength

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A three-point bending test was carried out on samples with a width of 3mm, a height of 3mm, and a length of 40mm. The test conditions were as follows: the distance between supports was 20mm, the radius of a support stand was 3.2mm (1/8 inch), the radius of a pressurization wedge was 3.2mm (1/8 inch), and the testing rate was 2 mm/min. Autograph AG-100KG equipment made by Shimadzu Manufacturing was used for measuring the flexural strain. The Flexural Strength (modulus of rupture) at the time of failure was computed from the stress-strain curve.

25

Flexural Strain

Maximum flexural strain at the time of fracture was computed from the stress-strain curve.

30

Amount of wear (For the Seal Ring and the Mating Material)

A friction wear testing equipment was used wherein the thrust load and the sliding speed can be adjusted, was used. The test sample of the seal ring had with an inner diameter

of $\phi 30\text{mm}$ (a width of 2mm, a thickness of 4mm, the joint of 2mm). The mating material was the aluminum alloy for die-casting, ADC12. A surface pressure of 2MPa and a speed of 6 m/s were maintained at room temperature.

Automatic transmission fluid was used for lubrication environment.

5 The test was conducted for 7 hours and the amount of wear of the mating material at the end of the test was computed from the difference between the cross sections of the test sample before and after the test. The amount of wear for the seal ring was calculated by measuring the average radial thickness of the ring using a micrometer screw gauge.

Friction Coefficient

10 A friction wear testing equipment was used wherein the thrust load and the sliding speed can be adjusted, was used. The test sample of the seal ring had with an inner diameter of $\phi 30\text{mm}$ (a width of 2mm, a thickness of 4mm, the joint of 2mm). The mating material was the aluminum alloy for die-casting, ADC12. A surface pressure of 2MPa and a speed of 6 m/s were maintained at room temperature.

Automatic transmission fluid was used for lubrication environment.

15 The test was conducted for 7 hours and the friction coefficient of the flat surface was measured 1 hour before the end of the test.

Rate of Leakage of the Automatic Transmission Fluid

25 Seal rings of $\phi 60\text{mm}$ (a width of 2.3mm, a thickness of 2.3mm, joint of 0.5 mm) were attached to an automatic transmission assembly with a shaft made from aluminum (aluminum alloy for die-casting, ADC12) and the housing also made from aluminum (aluminum alloy for die-casting, ADC12), automatic transmission fluid was used as oil under a pressure of 1 MPa, and the rate of leakage (ml/min) at the oil temperature of 23°C to 150°C was measured.

CLAIMS

1. A composition comprising:

- (a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole, copolymers of fluoropolymer and compatible blends thereof;
- (b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and
- (c) optionally, a fiber selected from the group consisting of aramid fiber, glass fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%, wherein said polymer is a polyimide, wherein said polyimide is prepared by a condensation polymerization reaction of an aromatic tetracarboxylic dianhydride or derivative thereof, and a diamine or derivative thereof, wherein said aromatic tetracarboxylic dianhydride is selected from the group consisting of pyromellitic dianhydride, biphenyl tetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, and combinations thereof; and wherein said diamine is selected from the group consisting of 4, 4'-diamino diphenyl ether, 3,4'-diamino diphenyl ether, p-phenylene diamine, m-phenylene diamine, and combinations thereof;

OR

wherein said polyimide is made from pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA);

OR

wherein said polyimide is a copolymer of polyimide derived from 3,3',4,4'-biphenyl tetracarboxylic dianhydride with p-phenylene diamine and/or m-phenylene diamine.

2. The composition as recited in claim 1, wherein the bulk density of said graphite additive material is at least about 0.20 g/cm³.
3. The composition as recited in claim 1, wherein the range of said average particle size of said graphite additive material is selected from the group consisting of less than 95 microns, less than 90 microns, less than 85 microns, less than 80 microns, less than 75 micron, less than 70 microns, less than 65 microns, less than 60 microns, less than 55 microns, less than 50 microns, less than 45 microns, less than 40 microns, less than 35 microns, less than 30 microns, less than 25 microns, less than 20 microns, less than 15 microns, and less than 10 microns.
4. The composition as recited in claim 1, wherein said fiber is aramid fiber.
5. The composition as recited in claim 4, wherein said aramid fiber is poly(p-phenylene terephthalamide).
6. An article comprising a matrix resin material, said matrix resin material having a composition comprising:
 - (a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole, copolymers of fluoropolymer and compatible blends thereof;

- (b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about $1.0 \text{ m}^2/\text{g}$ to about $10 \text{ m}^2/\text{g}$, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and
- (c) optionally, a fiber selected from the group consisting of aramid fiber, glass fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%.

7. The article as recited in claim 5, wherein said polymer is a polyimide, wherein said polyimide is prepared by a condensation polymerization reaction of an aromatic tetracarboxylic dianhydride or derivative thereof, and diamine or derivative thereof, wherein said aromatic tetracarboxylic dianhydride is selected from the group consisting of pyromellitic dianhydride, biphenyl tetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, and combinations thereof; and wherein said diamine is selected from the group consisting of 4,4'-diamino diphenyl ether, 3,4'-diamino diphenyl ether, p-phenylene diamine, m-phenylene diamine, and combinations thereof;

OR

wherein said polyimide is made from pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA);

OR

wherein said polyimide is a copolymer of polyimide derived from 3,3',4,4'-biphenyl tetracarboxylic dianhydride with p-phenylene diamine and/or m-phenylene diamine.

8. The article as recited in claim 6, wherein the bulk density of said graphite additive material is at least about 0.20 g/cm^3 .

9. The article as recited in claim 7, wherein the range of said average particle size of said graphite additive material is selected from the group consisting of less than 95 microns, less than 90 microns, less than 85 microns, less than 80 microns, less than 75 micron, less than 70

microns, less than 65 microns, less than 60 microns, less than 55 microns, less than 50 microns, less than 45 microns, less than 40 microns, less than 35 microns, less than 30 microns, less than 25 microns, less than 20 microns, less than 15 microns, and less than 10 microns.

10. The composition as recited in claim 6, wherein said fiber is aramid fiber.

11. The composition as recited in claim 10, wherein said aramid fiber is poly(p-phenylene terephthalamide).

12. An article as recited in claim 6, wherein said article is a seal ring.

13. The article as recited in claim 12, wherein said seal ring is placed in the space between a radial groove of a cylindrical member and a housing forming a bore in which said cylindrical member is movably positioned, said seal ring having a separation line to form opposing faces engaging to form a seal.

14. The article as recited in claim 12, wherein said seal ring having an outer surface free of scoring has a separation line, said separation line comprising a fracture through said ring's thickness to form opposing faces which are rough and mesh together such that when said faces are forced into contact, said faces are interlocked.

15. The article as recited in claim 14, wherein said separation line comprises a fracture joint, butt joint, step joint or scarf joint in the seal ring.

16. A process for making an article, said article comprising a matrix resin material, said matrix resin material having a composition comprising:

(a) a polymer selected from the group consisting of polyimide, polyester imide, polyester amide imide, polyamide imide, polyetherketone, polyetheretherketone, polyetherketoneketone, polyamide, liquid crystalline polyester, polyoxymethylene, polybenzimidazole, fluoropolymer, copolymers of polyimide, copolymers of polyester imide, copolymers of polyester amide imide, copolymers of polyamide imide, copolymers of polyetherketone, copolymers of polyetheretherketone, copolymers of polyetherketoneketone, copolymers of polyamide, copolymers of liquid crystalline

polyester, copolymers of polyoxymethylene, copolymers of polybenzimidazole
copolymers of fluoropolymer and compatible blends thereof;

(b) a graphite additive material, wherein said graphite additive material has a specific surface area in the range of from about 1.0 m²/g to about 10 m²/g, wherein said additive material has an average particle size less than about 100 microns, wherein particles of said graphite additive material having a rounded shape, and wherein the percent weight of said graphite additive material is in the range of from about 35% to about 70% of the total weight said composition; and

(c) optionally, a fiber selected from the group consisting of aramid fiber, glass fiber, carbon fiber, and mixtures thereof, wherein the percent weight of said fiber is in the range of from about 0% to about 10%; wherein said article is made by a process selected from the group consisting of powder compression, compression molding, extrusion molding, injection molding and reaction injection molding.

17. The process as recited in claim 16, wherein said polymer is a polyimide, wherein said polyimide is prepared by a condensation polymerization reaction of an aromatic tetracarboxylic dianhydride or derivative thereof, and a diamine or derivative thereof, wherein said acid anhydride is selected from group consisting of pyromellitic dianhydride, biphenyl tetracarboxylic acid dianhydride, benzophenone tetracarboxylic acid dianhydride, and combinations thereof; and wherein said diamine is selected from the group consisting of 4,4'-diamino diphenyl ether, 3,4'-diamino diphenyl ether, p-phenylene diamine, m-phenylene diamine, and combinations thereof;

OR

wherein said polyimide is made from pyromellitic acid dianhydride (PMDA) and 4,4'-oxydianiline (ODA);

OR

wherein said polyimide is a copolymer of polyimide derived from 2,3,3',4'-biphenyl tetracarboxylic dianhydride with p-phenylene diamine and/or m-phenylene diamine.

18. The process as recited in claim 16, wherein said article is a seal ring.