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(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **AUMAN, Brian, C.** [US/US]; 13436 Silver Brook Drive, Pickerington, Ohio 43147 (US). **DUNBAR, Meredith, L.** [US/US]; 69 N. Trine Street, Canal Winchester, Ohio 43110 (US). **HE, Tao** [US/US]; 104 Shrewsbury Drive, Wilmington, Delaware 19810 (US). **KOURTAKIS, Kostantinos** [US/US]; 804 Springlawn Drive, Media, Pennsylvania 19063 (US).

(74) Agent: **HALERZ, Traci**; E. I. Du Pont De Nemours And Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

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(54) Title: COVERLAY COMPOSITIONS AND METHODS RELATING THERETO

(57) Abstract: The present disclosure is directed to a coverlay comprising a polyimide film and an adhesive layer. The polyimide film is composed of a polyimide and a sub-micron filler. The polyimide is derived from at least one aromatic dianhydride component selected from rigid rod dianhydride, non-rigid rod dianhydride and combinations thereof, and at least one aromatic diamine component selected from rigid rod diamine, non-rigid rod diamine and combinations thereof. The mole ratio of dianhydride to diamine is 48-52:52-48 and the ratio of X:Y is 20-80:80-20 where X is the mole percent of rigid rod dianhydride and rigid rod diamine, and Y is the mole percent of non-rigid rod dianhydride and non-rigid rod diamine. The sub-micron filler is less than 550 nanometers in at least one dimension; has an aspect ratio greater than 3:1; is less than the thickness of the film in all dimensions.



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TITLE

COVERLAY COMPOSITIONS AND METHODS RELATING THERETO

FIELD OF DISCLOSURE

5 The present disclosure relates generally to a coverlay. More specifically the coverlay comprises a polyimide film and an adhesive layer. The polyimide film comprises a sub-micron filler and a polyimide polymer having a hybrid backbone structure.

BACKGROUND OF THE DISCLOSURE

10 A coverlay is used as a protective cover film for flexible printed circuit boards, electronic components and the leadframe of an integrated circuit package. The coverlay can prevent damage from scratches, oxidation and contamination.

15 Coverlays need to have good electrical properties (e.g., dielectric strength), as well as acceptable structural properties for security against unwanted visual inspection and tampering of the electronic components protected by the coverlay.

20 A need exists for a low cost coverlay having improved thermal and dimensional stability.

SUMMARY OF THE INVENTION

The present disclosure is directed to coverlay comprises a polyimide film and an adhesive layer. The polyimide film is derived from:

- 25 i) at least one aromatic dianhydride component selected from the group consisting of rigid rod dianhydride, non-rigid rod dianhydride and combinations thereof, and
- ii) at least one aromatic diamine component selected from the group consisting of rigid rod diamine, non-rigid rod diamine
- 30 and combinations thereof.

The mole ratio of dianhydride to diamine is 48-52:52-48 and the ratio of X:Y is 20-80:80-20 where X is the mole percent of rigid rod dianhydride

and rigid rod diamine, and Y is the mole percent of non-rigid rod dianhydride and non-rigid rod diamine based upon the total dianhydride component and total diamine component of the polyimide. The polyimide film also comprises a sub-micron filler that is less than 550 nanometers
5 (as a numerical average) in at least one dimension, has an aspect ratio greater than 3:1, is less than the polyimide film thickness in all dimensions, and is present in an amount from 10 to 45 volume percent of the polyimide film. The polyimide film has a thickness from 5 to 150 microns.

The adhesive layer is selected from polyimide resins, epoxy resins,
10 phenolic resins, melamine resins, acrylic resins, cyanate resins or combinations thereof.

DETAILED DESCRIPTION

Definitions

15 "Film" is intended to mean a free-standing film or a coating on a substrate. The term "film" is used interchangeably with the term "layer" and refers to covering a desired area.

"Dianhydride" as used herein is intended to include precursors or derivatives thereof, which may not technically be a dianhydride but would
20 nevertheless functionally equivalent due to the capability of reacting with a diamine to form a polyamic acid which in turn could be converted into a polyimide.

"Diamine" as used herein is intended to include precursors or derivatives thereof, which may not technically be diamines but are
25 nevertheless functionally equivalent due to the capability of reacting with a dianhydride to form a polyamic acid which in turn could be converted into a polyimide.

"Polyamic acid" as used herein is intended to include any polyimide precursor material derived from a combination of dianhydride and diamine
30 monomers or functional equivalents thereof and capable of conversion to a polyimide.

"Sub-micron" is intended to describe particles having (as a numerical average) at least one dimension that is less than a micron.

“Chemical conversion” or “chemically converted” as used herein denotes the use of a catalyst (accelerator) or dehydrating agent (or both) to convert the polyamic acid to polyimide and is intended to include a partially chemically converted polyimide which is then dried at elevated
5 temperatures to a solids level greater than 98%.

“Aspect ratio” is intended to mean a ratio of one dimension to another, such as a ratio of length to height.

In describing certain polymers it should be understood that sometimes applicants are referring to the polymers by the monomers used to make them or the amounts of the monomers used to make them. While
10 such a description may not include the specific nomenclature used to describe the final polymer or may not contain product-by-process terminology, any such reference to monomers and amounts should be interpreted to mean that the polymer is made from those monomers,
15 unless the context indicates or implies otherwise.

As used herein, the terms “comprises,” “comprising,” “includes,” “including,” “has,” “having” or any other variation thereof, are intended to cover a non-exclusive inclusion. For Example, a method, process, article, or apparatus that comprises a list of elements is not necessarily limited to
20 only those elements but may include other elements not expressly listed or inherent to such method, process, article, or apparatus. Further, unless expressly stated to the contrary, “or” refers to an inclusive or and not to an exclusive or. For Example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is
25 false (or not present) and B is true (or present), and both A and B are true (or present).

Also, articles “a” or “an” are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to
30 include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

Overview

The coverlay comprises a polyimide film and an adhesive layer. The polyimide film of the present disclosure comprises a polyimide and a sub-micron filler. The sub-micron filler of the present disclosure can generally be incorporated into the polyimide of the present disclosure at
5 relatively high loadings without causing the polyimide film to be unduly brittle while maintaining or decreasing coefficient of thermal expansion and increasing storage modulus. The polyimide has a hybrid backbone structure comprising rigid rod portions and non-rigid rod portions.

10 Polyimide

The polyimides of the present disclosure are derived from the polymerization reaction of certain aromatic dianhydrides with certain aromatic diamines to provide a polymeric backbone structure that comprises both rigid rod portions and non-rigid rod portions. The rigid rod
15 portions arise from the polymerization of aromatic rigid rod monomers into the polyimide, and the non-rigid rod portions arise from the polymerization of non-rigid rod aromatic monomers into the polyimide. Aromatic rigid rod monomers give a co-linear (about 180°) configuration to the polymer backbone, and therefore relatively little movement capability, when
20 polymerized into a polyimide.

Examples of aromatic rigid rod diamine monomers are:

1,4-diaminobenzene (PPD),
4,4'-diaminobiphenyl,
2,2'-bis(trifluoromethyl) 4,4'-diaminobiphenyl (TFMB),
25 1,4-naphthalenediamine,
1,5-naphthalenediamine,
4,4"-diamino terphenyl,
4,4'-diamino benzanilide
4,4'-diaminophenyl benzoate,
30 3,3'-dimethyl-4,4'-diaminobiphenyl,
2,5-diaminotoluene, and
the like.

Examples of aromatic rigid rod dianhydride monomers are:

pyromellitic dianhydride (PMDA),

2,3,6,7-naphthalenetetracarboxylic dianhydride, and

3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA).

5

Monomers having a freedom of rotational movement or bending (once polymerized into a polyimide) substantially equal to or less than the above Examples (of rigid rod diamines and rigid rod dianhydrides) are intended to be deemed rigid rod monomers for purposes of this disclosure.

10

Non-rigid rod monomers for purposes of this disclosure are intended to mean aromatic monomers capable of polymerizing into a polyimide backbone structure having substantially greater freedom of movement compared to the rigid rod monomers described and exemplified above. The non rigid rod monomers, when polymerized into a polyimide, provide a backbone structure having a bend or otherwise are not co-linear along the polyimide backbone they create (e.g., are not about 180°).

15

Examples of non-rigid rod monomers in accordance with the present disclosure include any diamine and any dianhydride capable of providing a rotational or bending bridging group along the polyimide backbone.

20

Examples of rotational or bending bridging groups include -O-, -S-, -SO₂-, -C(O)-, -C(CH₃)₂-, -C(CF₃)₂-, and -C(R,R')- where R and R' are the same or different and are any organic group capable of bonding to a carbon.

25

Examples of non-rigid rod diamines include: 4,4'-diaminodiphenyl ether ("ODA"), 2,2-bis-(4-aminophenyl) propane, 1,3-diaminobenzene (MPD), 4,4'-diaminobenzophenone, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfide, 4,4'-diaminodiphenyl sulfone, 3,3'-diaminodiphenyl sulfone, bis-(4-(4-aminophenoxy)phenyl sulfone (BAPS), 4,4'-bis-(aminophenoxy)biphenyl (BAPB), 3,4'-diaminodiphenyl ether, 4,4'-diaminobenzophenone, 4,4'-isopropylidenedianiline, 2,2'-bis-(3-aminophenyl)propane, N,N-bis-(4-aminophenyl)-n-butylamine, N,N-bis-(4-aminophenyl) methylamine, m-amino benzoyl-p-amino anilide, 4-aminophenyl-3-aminobenzoate, N,N-bis-(4-aminophenyl) aniline, 2,4-

30

diaminotoluene, 2,6-diaminotoluene, 2,4-diamine-5-chlorotoluene, 2,4-
 diamino-6-chlorotoluene, 2,4-bis-(beta-amino-t-butyl) toluene, bis-(p-beta-
 amino-t-butyl phenyl) ether, p-bis-2-(2-methyl-4-aminopentyl) benzene, m-
 xylylene diamine, p-xylylene diamine. 1,2-bis-(4-aminophenoxy)benzene,
 5 1,3-bis-(4-aminophenoxy) benzene, 1,2-bis-(3-aminophenoxy)benzene,
 1,3-bis-(3-aminophenoxy) benzene, 1-(4-aminophenoxy)-3-(3-
 aminophenoxy) benzene, 1,4-bis-(4-aminophenoxy) benzene, 1,4-bis-(3-
 aminophenoxy) benzene, 1-(4-aminophenoxy)-4-(3-aminophenoxy)
 benzene, 2,2-bis-(4-[4-aminophenoxy]phenyl) propane (BAPP), 2,2'-bis-(4-
 10 aminophenyl)-hexafluoro propane (6F diamine), 2,2'-bis-(4-phenoxy
 aniline) isopropylidene, 4,4'-diamino-2,2'-trifluoromethyl diphenyloxide,
 3,3'-diamino-5,5'-trifluoromethyl diphenyloxide, 4,4'-trifluoromethyl-2,2'-
 diaminobiphenyl, 2,4,6-trimethyl-1,3-diaminobenzene, 4,4'-oxy-bis-[2-
 trifluoromethyl)benzene amine] (1,2,4-OBABTF), 4,4'-oxy-bis-[3-
 15 trifluoromethyl)benzene amine], 4,4'-thio-bis-[(2-trifluoromethyl)benzene-
 amine], 4,4'-thiobis[(3-trifluoromethyl)benzene amine], 4,4'-sulfoxyl-bis-[(2-
 trifluoromethyl)benzene amine, 4,4'-sulfoxyl-bis-[(3-
 trifluoromethyl)benzene amine], and 4,4'-keto-bis-[(2-
 trifluoromethyl)benzene amine].

20 Examples of non-rigid rod aromatic dianhydrides include 2,2',3,3'-
 benzophenone tetracarboxylic dianhydride, 2,3,3',4'-benzophenone
 tetracarboxylic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic
 dianhydride (BTDA), 2,2',3,3'-biphenyl tetracarboxylic dianhydride,
 2,3,3',4'-biphenyl tetracarboxylic dianhydride, 4,4'-thio-diphthalic
 25 anhydride, bis (3,4-dicarboxyphenyl) sulfone dianhydride (DSDA), bis (3,4-
 dicarboxyphenyl) sulfoxide dianhydride, 4,4'-oxydiphthalic anhydride
 (ODPA), bis (3,4-dicarboxyphenyl) thio ether dianhydride, 2,2-Bis[4-(3,4-
 dicarboxyphenoxy)phenyl]propane dianhydride (BPADA), bisphenol S
 dianhydride, 2,2-bis-(3,4-dicarboxyphenyl) 1,1,1,3,3,3,-hexafluoropropane
 30 dianhydride (6FDA), 5,5-[2,2,2]-trifluoro-1-(trifluoromethyl)ethylidene, bis-
 1,3-isobenzofurandione, bis (3,4-dicarboxyphenyl) methane dianhydride,
 cyclopentadienyl tetracarboxylic acid dianhydride, ethylene tetracarboxylic
 acid dianhydride, 2,2-bis(3,4-dicarboxyphenyl) propane dianhydride.

In some embodiments, the mole ratio of dianhydride to diamine is 48-52:52-48 and the ratio of X:Y is 20-80:80-20 where X is the mole percent of rigid rod dianhydride and rigid rod diamine, and Y is the mole percent of non-rigid rod dianhydride and non-rigid rod diamine based upon the total dianhydride component and diamine component of the polyimide. And in alternative embodiments can be any sub-range within that broad ratio (e.g., 20-80 includes any range between and optionally including 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75 and 80, and 80-20 includes any range between and optionally including 80, 75, 70, 65, 60, 55, 45, 40, 35, 30, and 25).

In one embodiment, the polyimide of the present disclosure is derived from substantially equal molar amounts of 4,4'-diaminodiphenyl ether (4,4'-ODA) non-rigid rod monomer, and pyromellitic dianhydride (PMDA), rigid rod monomer. In another embodiment, at least 70 mole percent of the aromatic dianhydride component is pyromellitic dianhydride; and at least 70 mole percent of the aromatic diamine component is 4,4'-diaminodiphenyl ether. In some embodiments, at least 70, 75, 80, 85, 90 or 95 mole percent of the aromatic dianhydride component is pyromellitic dianhydride (based upon total dianhydride content of the polyimide); and at least 70, 75, 80, 85, 90 or 95 mole percent of the aromatic diamine component is 4,4'-diaminodiphenyl ether (based upon total diamine content of the polyimide). Such PMDA//4,4'-ODA polyimides have been found to be particularly well suited for combination with the sub-micron fillers of the present disclosure, for improved properties at a relatively low cost. In another embodiment, the polyimide is derived from 100 mole percent pyromellitic dianhydride and 100 mole percent 4,4'-diaminodiphenyl ether. In another embodiment, the polyimide is a random copolymer derived from 4,4'-diaminodiphenyl ether and 1,4-diaminobenzene with pyromellitic dianhydride and 3,3',4,4'-biphenyl tetracarboxylic dianhydride. In yet another embodiment, the polyimide is a random copolymer derived from 4,4'-diaminodiphenyl ether and 1,4-diaminobenzene with pyromellitic dianhydride.

In another embodiment, at least 75 mole percent of the aromatic dianhydride component is pyromellitic dianhydride and 70 mole percent 4,4'-diaminodiphenyl ether and 30 mole percent 1,4-diaminobenzene as the aromatic diamine component.

5 In another embodiment, the polyimide is a block copolymer. A block copolymer is a polymer in which there are sequences of substantially one dianhydride/diamine combination along the polymer backbone as opposed to a completely random distribution of monomer sequences. Typically this is achieved by sequential addition of different
10 monomers during the polyamic acid preparation.

In yet another embodiment, the polyimide is block copolymer derived from 4,4'-diaminodiphenyl ether and 1,4-diaminobenzene with pyromellitic dianhydride. In yet another embodiment, the polyimide is a block copolymer is derived from 4,4'-diaminodiphenyl ether (4,4'-ODA)
15 and 1,4-diaminobenzene (PPD) with pyromellitic dianhydride (PMDA) and 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA). In yet another embodiment, the polyimide is a block copolymer consisting of substantially rigid blocks (PMDA reacted with PPD) and substantially more flexible blocks (PMDA reacted with ODA). In another embodiment, the block
20 copolymer is derived from 10 to 40 mole percent blocks of pyromellitic dianhydride and 1,4-diaminobenzene and from 90 to 60 mole percent blocks of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

Sub-Micron Filler

25 In accordance with the present disclosure, the filler is a sub-micron (in at least one dimension) filler or a mixture of sub-micron fillers.

In one embodiment, the polyimide film of the present disclosure comprises at least one sub-micron filler, the sub-micron filler:

1. being less than 550 nanometers (and in some embodiments,
30 less than 475, 450, 425, 400, 375, 350, 325, 300, 275, 250, 225, or 200 nanometers) in at least one dimension (since fillers can have a variety of shapes in any dimension and since filler shape can vary along any dimension, the "at

least one dimension" is intended to be a numerical average along that dimension);

- 5
2. having an average aspect ratio greater than 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 to 1;
 3. being less than 100, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15 or 10 percent of the polyimide film thickness in all dimensions; and
 - 10 4. being present in an amount between and optionally including any two of the following percentages: 10, 15, 20, 25, 30, 35, 40, and 45 volume percent of the polyimide film.

Suitable sub-micron fillers are generally stable at temperatures
15 above 300, 350, 400, 425 or 450°C, and in some embodiments do not significantly decrease the electrical insulation properties of the polyimide polyimide film. In some embodiments, the sub-micron filler is selected from a group consisting of needle-like fillers (acicular), fibrous fillers, platelet fillers and mixtures thereof. In one embodiment, the sub-micron
20 filler is substantially non-aggregated. The sub-micron filler can be hollow, porous, or solid.

In one embodiment, the sub-micron fillers of the present disclosure exhibit an aspect ratio of at least 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, or 15 to 1. In one embodiment, the sub-micron filler aspect ratio is 5:1 or
25 greater. In another embodiment, the sub-micron filler aspect ratio is 10:1 or greater, and in another embodiment, the aspect ratio is 12:1 or greater. In some embodiments, the sub-micron filler is selected from a group consisting of oxides (e.g., oxides comprising silicon, magnesium and/or aluminum), nitrides (e.g., nitrides comprising boron and/or silicon),
30 carbides (e.g., carbides comprising tungsten and/or silicon) and combinations thereof. In some embodiments, the sub-micron filler is acicular titanium dioxide, talc, SiC fiber, platy Al₂O₃ or mixtures thereof. In

some embodiments, the sub-micron filler is less than (as a numerical average) 50, 25, 20, 15, 12, 10, 8, 6, 5, 4, or 2 microns in all dimensions.

In yet another embodiment, carbon fiber and graphite can be used in combination with other sub-micron fillers to increase mechanical properties. However in one embodiment, the loading of graphite, carbon fiber and/or electrically conductive fillers may need to be below the percolation threshold (perhaps less than 10 volume percent), since graphite and carbon fiber fillers can diminish electrical insulation properties and in some embodiments, diminished electrical insulation properties are not desirable.

In some embodiments, the sub-micron filler is coated with a coupling agent. In some embodiments, the sub-micron filler is coated with an aminosilane coupling agent. In some embodiments, the sub-micron filler is coated with a dispersant. In some embodiments, the sub-micron filler is coated with a combination of a coupling agent and a dispersant. Alternatively, the coupling agent and/or dispersant can be incorporated directly into the polyimide film and not necessarily coated onto the sub-micron filler. In some embodiments, the sub-micron filler comprises a acicular titanium dioxide, at least a portion of which is coated with an aluminum oxide.

In some embodiments, the sub-micron filler is chosen so that it does not itself degrade or produce off-gasses at the desired processing temperatures. Likewise in some embodiments, the sub-micron filler is chosen so that it does not contribute to degradation of the polymer.

In one embodiment, filler composites (e.g. single or multiple core/shell structures) can be used, in which one oxide encapsulates another oxide in one particle.

Polyimide Film

It has been discovered that relatively less expensive polyimides can be filled with sub-micron filler of the present disclosure and thereby perform, at least in some ways, more similarly to more expensive polyimides, but at a much lower cost. More expensive monomers such as

BPDA or fluorinated monomers can at least in part (or entirely) be replaced with less expensive monomers. In addition to expensive monomers, some polyimides are more difficult to process commercially, such as BPDA//PPD due to blistering. Lower production rates drive up the cost of the film. Additionally, polyimides derived from all rigid rod monomers may have low CTE and high modulus but when filled have low elongation. It has been found that the submicron fillers that have an aspect ratio of 3:1 or greater can be incorporated at relatively high loading levels (10 to 45 volume percent) into less expensive, easily processable polyimides. The sub-micron filler of the present disclosure tends to increase the storage modulus and decrease or approximately maintain the CTE of the polyimide film of the present disclosure with out causing the polyimide film to become unduly brittle.

It is surprising that the sub-micron filler of the present disclosure may not behave in the same manner in all polyimides. Surprisingly in a rigid rod polyimide (BPDA//PPD) the CTE may be greater than in unfilled rigid rod polyimide.

The sub-micron filler of the present disclosure, when incorporated into the polyimides of the present disclosure, produce polyimide films having better properties (or balance of properties) compared to their conventional non-high aspect ratio (less than 3:1 aspect ratio) counterparts.

In some embodiments, the polyimide film comprises a polyimide derived from 100 mole percent of pyromellitic dianhydride as the aromatic dianhydride component; and 100 mole percent 4,4'-diaminodiphenyl ether as the aromatic diamine component and the sub-micron filler is acicular titanium dioxide, talc, SiC fiber, platy Al₂O₃ or mixture thereof. In some embodiments, the polyimide is a homopolymer of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

In another embodiment, the polyimide film comprises a polyimide wherein the polyimide is block copolymer derived from: 10 to 40 mole percent blocks of pyromellitic dianhydride and 1,4 diaminobenzene; from 90 to 60 mole percent blocks of pyromellitic dianhydride and

4,4'-diaminodiphenyl ether and the sub-micron filler is acicular titanium dioxide, talc or mixture thereof.

Thermal and Dimensional Stability

5 While it is generally known that the addition of filler will decrease CTE and increase storage modulus, it is surprising, that for the sub-micron fillers of the present disclosure, there is a threshold above which a significant increase in storage modulus and/or a decrease in CTE is observed. In one embodiment, the sub-micron filler will substantially
10 maintain (within 80, 70, 60, 50, 40, 30, 20, 10, 5, 4, 3, 2, or 1 percent, plus or minus) the coefficient of thermal expansion (CTE) while improving mechanical and thermal properties.

 In one embodiment, the polyimide films of the present disclosure have an in-plane CTE in a range between (and optionally including) any
15 two of the following: 1, 5, 10, 15, 20, 25, 30 and 35 ppm/°C, where the in-plane coefficient of thermal expansion (CTE) is measured between 60°C (or 50°C) and 350°C.

 Some unfilled block or random copolymers of the present disclosure can have a relatively low CTE. Thus, in some embodiments,
20 sub-micron fillers of the present disclosure have little impact on a block copolymer CTE. In some embodiments, the sub-micron fillers of the present disclosure may increase the CTE of block or random copolymers having a low CTE but the CTE is still maintained in a desirable range. The thickness of a polyimide film can also impact CTE, where thinner films
25 tend to give a lower CTE (and thicker films, a higher CTE), and therefore, polyimide film thickness can be used to fine tune polyimide film CTE, depending upon any particular application selected. The polyimide films of the present disclosure have a thickness in a range between (and optionally including) any of the following thicknesses (in microns): 5, 6, 8,
30 10, 12, 15, 20, 25, 50, 75, 100, 125 and 150 microns. Monomers and sub-micron fillers within the scope of the present disclosure can also be selected or optimized to fine tune CTE within the above range. Ordinary skill and experimentation may be necessary in fine tuning any particular

CTE of the polyimide films of the present disclosure, depending upon the particular application. In some embodiments, the in-plane CTE of the polyimide film can be obtained by thermomechanical analysis utilizing a TA Instruments TMA-2940 run at 10°C/min, up to 400°C, then cooled and reheated to 400°C, with the CTE in ppm/°C obtained during the reheat scan between 50°C and 350°C. In another embodiment, the in-plane CTE of the film can be obtained by Thermal Mechanical Analysis (TA Instruments, TMA-2940, heat 10°C/min, up to 460°C, then cooled and reheat to 500°C) was evaluated between 50-350°C on the reheat. In another embodiment, the in-plane CTE of the film can be obtained by Thermal Mechanical Analysis (TA Instruments, TMA-2940, heat 10°C/min, up to 380°C, then cooled and reheated to 380°C) and evaluated between 50-350°C on the reheat.

In some embodiments, the sub-micron filler increases the storage modulus above the glass transition temperature (T_g) of the polyimide. In some embodiments, the sub-micron filler of the present disclosure increases the storage modulus at 25°C at least 20, 22, 24, 26, 28 or 30% compared to sub-micron filler having an aspect ratio less than 3:1. In some embodiments, the sub-micron filler of the present disclosure increases the storage modulus at 480°C to 500°C at least 40, 42, 44 or 46% compared to sub-micron filler having an aspect ratio less than 3:1. In some embodiments, the sub-micron filler of the present disclosure increases the storage modulus at 25°C at least 38, 40, 42, 44 or 46% compared to unfilled polyimide. In some embodiments, the sub-micron filler of the present disclosure increases the storage modulus at 480°C to 500°C at least 52, 53, 54 or 55% compared to unfilled polyimide.

Typically, as the amount of filler increases in a film, the more brittle and difficult to process the film tends to become. Typically when tensile elongation is less than 20 percent, films are difficult to process, thus, are of limited commercial value. It is surprising that when the sub-micron fillers of the present disclosure are added to a polyimide having a mole ratio of dianhydride to diamine of 48-52:52-48 and the ratio of X:Y is 20-80:80-20 where X is the mole percent of rigid rod dianhydride and rigid

rod diamine, and Y is the mole percent of non-rigid rod dianhydride and non-rigid rod diamine, the tensile elongation remains acceptable. In some embodiments, the tensile elongation remains acceptable when greater than 10 volume percent of the sub-micron filler is used. In one
5 embodiment, the tensile elongation remains acceptable when greater than 30 volume percent of the sub-micron filler is used. In yet another embodiment, the tensile elongation remains acceptable when greater than 40 volume percent of the sub-micron filler is used.

Generally, when forming the polyimide, a chemical conversion
10 process (as opposed to a thermal conversion process) will provide a lower CTE polyimide film. Thus, while the advantages of the present disclosure can be seen for both chemically or thermally converted polyimides, the advantages of incorporating the sub-micron filler of the present disclosure may be most useful for chemically converted polyimides of the present
15 disclosure.

Polyimide Film Formation

Polyimide films of the present disclosure can be made by methods well known in the art. In some embodiments, the polyimide polyimide film
20 can be produced by combining the above monomers together with a solvent to form a polyamic acid (also called a polyamide acid solution). The dianhydride and diamine components are typically combined in a molar ratio of aromatic dianhydride component to aromatic diamine component of from 0.90 to 1.10. Molecular weight can be adjusted by
25 adjusting the molar ratio of the dianhydride and diamine components.

Chemical or thermal conversion can be used in the practice of the present disclosure. In instances where chemical conversion is used, a polyamic acid casting solution is derived from the polyamic acid solution. In one embodiment, the polyamic acid casting solution comprises the
30 polyamic acid solution combined with conversion chemicals, such as: (i) one or more dehydrating agents, such as, aliphatic acid anhydrides (acetic anhydride, etc.) and aromatic acid anhydrides; and (ii) one or more catalysts, such as, aliphatic tertiary amines (triethylamine, etc.), aromatic

tertiary amines (dimethylaniline, etc) and heterocyclic tertiary amines (pyridine, picoline, isoquinoline, etc). The anhydride dehydrating material is often used in a molar excess of the amount of amide acid groups in the copolyamic acid. The amount of acetic anhydride used is typically about
5 2.0-3.0 moles per equivalent of amide acid. Generally, a comparable amount of tertiary amine catalyst is used.

In one embodiment, the polyamic acid is dissolved in an organic solvent at a concentration from about 5 weight percent up to and including 40 weight percent. In one embodiment, the polyamic acid is dissolved in
10 an organic solvent at a concentration of about 5, 10, 15, 20, 25, 30, 35 or 40 weight percent. Examples of suitable solvents include: formamide solvents (N,N-dimethylformamide, N,N-diethylformamide, etc.), acetamide solvents (N,N-dimethylacetamide, N,N-diethylacetamide, etc.), pyrrolidone solvents (N- methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, etc.), phenol
15 solvents (phenol, o-, m- or p-cresol, xlenol, halogenated phenols, catechol, etc.), hexamethylphosphoramide and gamma-butyrolactone. It is desirable to use one of these solvents or mixtures thereof. It is also possible to use combinations of these solvents with aromatic hydrocarbons such as xylene and toluene, or ether containing solvents like
20 diglyme, propylene glycol methyl ether, propylene glycol, methyl ether acetate, tetrahydrofuran, and the like.

In one embodiment, the prepolymer can be prepared and combined with the sub-micron filler (dispersion or colloid thereof) using numerous variations to form the polyimide film of this disclosure. "Prepolymer" is
25 intended to mean a lower molecular weight polymer, typically made with a small stoichiometric excess (about 2 to 4%) of diamine monomer (or excess dianhydride monomer). Increasing the molecular weight (and solution viscosity) of the prepolymer can be accomplished by adding incremental amounts of additional dianhydride (or additional diamine, in
30 the case where the dianhydride monomer is originally in excess in the prepolymer) in order to approach a 1:1 stoichiometric ratio of dianhydride to diamine.

Useful methods for producing polyimide film in accordance with the present disclosure can be found in U.S. 5,166,308 to Kreuz, et al. Numerous variations are also possible, such as: (a) a method wherein the diamine components and dianhydride components are preliminarily mixed together and then the mixture is added in portions to a solvent while stirring, (b) a method wherein a solvent is added to a stirring mixture of diamine and dianhydride components (contrary to (a) above), (c) a method wherein diamines are exclusively dissolved in a solvent and then dianhydrides are added thereto at such a ratio as allowing to control the reaction rate, (d) a method wherein the dianhydride components are exclusively dissolved in a solvent and then amine components are added thereto at such a ratio to allow control of the reaction rate, (e) a method wherein the diamine components and the dianhydride components are separately dissolved in solvents and then these solutions are mixed in a reactor, (f) a method wherein the polyamic acid with excessive amine component and another polyamic acid with excessive dianhydride component are preliminarily formed and then reacted with each other in a reactor, particularly in such a way as to create a non-random or block copolymer, (g) a method wherein a specific portion of the amine components and the dianhydride components are first reacted and then the residual diamine components are reacted, or vice versa, (h) a method wherein the conversion chemicals are mixed with the polyamic acid to form a polyamic acid casting solution and then cast to form a gel film, (i) a method wherein the components are added in part or in whole in any order to either part or whole of the solvent, also where part or all of any component can be added as a solution in part or all of the solvent, (j) a method of first reacting one of the dianhydride components with one of the diamine components giving a first polyamic acid, then reacting the other dianhydride component with the other amine component to give a second polyamic acid, and then combining the amic acids in any one of a number of ways prior to film formation, and (k) a method of creating block copolymers by sequential addition, e.g., adding a first diamine and a first dianhydride to form a polyamic acid having excess dianhydride (or excess

diamine) to create a first block and then adding a second diamine and a second dianhydride to the polyamic acid to form a second block in the presence of the first block; alternatively, blocks can be made based upon different dianhydrides (and the same diamine) or based upon different dianhydrides and different diamines (in each block), depending upon the particular application or properties desired.

The sub-micron filler (dispersion or colloid thereof) can be added at several points in the polyimide film preparation. In one embodiment, the colloid or dispersion is incorporated into a prepolymer to yield a Brookfield solution viscosity in the range of about 50-100 poise at 25°C. In an alternative embodiment, the colloid or dispersion can be combined with the monomers directly, and in this case, polymerization occurs with the filler present during the reaction. The monomers may have an excess of either monomer (diamine or dianhydride) during this "in situ" polymerization. The monomers may also be added in a 1:1 ratio. In the case where the monomers are added with either the amine (case i) or the dianhydride (case ii) in excess, increasing the molecular weight (and solution viscosity) can be accomplished, if necessary, by adding incremental amounts of additional dianhydride (case i) or diamine (case ii) to approach the 1:1 stoichiometric ratio of dianhydride to amine.

The polyamic acid casting solution can then be cast or applied onto a support, such as an endless belt or rotating drum. The polyamic acid contain conversion chemical reactants. Next, the solvent-containing film can be converted into a self-supporting film by baking at an appropriate temperature (thermal curing) to remove solvent or baking together with the chemical conversion reactants (chemical curing). The film can then be separated from the support, oriented such as by tentering, with continued thermal curing to provide a polyimide film.

Generally speaking, film smoothness may be desirable, since surface roughness: i. can interfere with the functionality of the layer or layers deposited on the polyimide film of the present disclosure, ii. can increase the probability of electrical or mechanical defects, and iii. can diminish property uniformity along the polyimide film. In one embodiment,

the sub-micron filler (and any other discontinuous domains) are sufficiently dispersed during film formation, such that the sub-micron filler (and any other discontinuous domains) are sufficiently between the surfaces of the polyimide film formation to provide a final polyimide film having an average surface roughness (Ra) of less than 1000, 750, 500 or 400 nanometers. Surface roughness as provided herein can be determined by optical surface profilometry to provide Ra values, such as, by measuring on a Veeco Wyco NT 1000 Series instrument in VSI mode at 25.4x or 51.2x utilizing Wyco Vision 32 software.

10 The polyamic acid (and casting solution) can further comprise any one of a number of additives, such as processing aids (e.g., oligomers), antioxidants, light stabilizers, flame retardant additives, anti-static agents, heat stabilizers, ultraviolet absorbing agents, fillers or various reinforcing agents.

15 An alkoxy silane coupling agent (or any conventional, nonconventional, presently known or future discovered coupling agent) can be added during the process by pretreating the sub-micron filler prior to formulation. Alkoxysilane coupling agents can also be added during the "in situ" polymerization by combining the fillers and monomers with the alkoxy silane, generally so long as the coupling agent does not interfere with the polymerization reaction.

20 In some cases, the dianhydride can be contacted with the sub-micron filler. While not intending to be bound to any particular theory or hypothesis, it is believed such contact between the dianhydride and the sub-micron filler can functionalize the sub-micron filler with the dianhydride prior to further reaction with the monomers or prepolymer. Ultimately, a filled polyamic acid composition is generally cast into a film, which is subjected to drying and curing (chemical and/or thermal curing) to form a filled polyimide film. Any conventional or non-conventional method of manufacturing filled polyimide films can be used in accordance with the present disclosure. The manufacture of filled polyimide films in general is well known and need not be further described here. In one embodiment, the polyimide used in polyimide film of the present disclosure has a high

glass transition temperature (T_g) of greater than 300, 310, 320, 330, 340, 350, 360, 370 380, 390 or 400°C. A high T_g generally helps maintain mechanical properties, such as storage modulus, at high temperatures.

In some embodiments, electrically insulating fillers may be added to
5 modify the electrical properties of the polyimide film. In some
embodiments, it is important that the polyimide film be free of pinholes or
other defects (foreign particles, gels, filler agglomerates or other
contaminates) that could adversely impact the electrical integrity and
dielectric strength of the polyimide film, and this can generally be
10 addressed by filtering. Such filtering can be done at any stage of the
polyimide film manufacture, such as, filtering solvated filler before or after
it is added to one or more monomers and/or filtering the polyamic acid,
particularly when the polyamic acid is at low viscosity, or otherwise,
filtering at any step in the manufacturing process that allows for filtering.
15 In one embodiment, such filtering is conducted at the minimum suitable
filter pore size or at a level just above the largest dimension of the
selected filler material. In some embodiments, the sub-micron filler is
subjected to intense dispersion energy, such as agitation and/or high
shear mixing or media milling or other dispersion techniques, including the
20 use of dispersing agents, when incorporated into the film (or incorporated
into a polyimide precursor) to inhibit unwanted agglomeration above the
desired maximum filler size or to break up aggregates which may be
originally present in the sub-micron filler. As the aspect ratio of the
sub-micron filler increases, so too does the tendency of the sub-micron
25 filler's long axis to align or otherwise position itself parallel to the outer
surfaces of the polyimide film.

A single layer film can be made thicker in an attempt to decrease
the effect of defects caused by unwanted (or undesirably large)
discontinuous phase material within the film. Alternatively, multiple layers
30 of polyimide may be used to diminish the harm of any particular defect
(unwanted discontinuous phase material of a size capable of harming
desired properties) in any particular layer, and generally speaking, such
multilayers will have fewer defects in performance compared to a single

polyimide layer of the same thickness. Using multiple layers of polyimide films can diminish or eliminate the occurrence of defects that may span the total thickness of the film, because the likelihood of having defects that overlap in each of the individual layers tends to be extremely small.

5 Therefore, a defect in any one of the layers is much less likely to cause an electrical or other type failure through the entire thickness of the film. In some embodiments, the polyimide film comprises two or more polyimide layers. In some embodiments, the polyimide layers are the same. In some
10 embodiments, the polyimide layers are different. In some embodiments, the polyimide layers independently may comprise a thermally stable filler, reinforcing fabric, inorganic paper, sheet, scrim or combinations thereof. Optionally, 0-55 weight percent of the film also includes other ingredients to modify properties as desired or required for any particular application.

15

Coverlay

The coverlay of the present disclosure comprises the above described polyimide film and an adhesive layer for maintaining the placement of the coverlay film once applied. In some embodiments, the
20 adhesive is a polyimide resin that can flow and bond at temperatures below the polyimide adhesive decomposition temperature. In one embodiment, the adhesive is a polyimide thermoplastic resin, optionally further comprising a thermosetting adhesive, such as, epoxy resin and/or phenolic resin. For adhesives having both thermoplastic and
25 thermosetting components, the content of the thermosetting resin in the adhesive layer generally ranges from 5 to 400 parts by weight, preferably from 50 to 200 parts by weight, per 100 parts by weight of resin components other than the thermosetting resin.

In some embodiments, the adhesive layer is selected from
30 polyimide resins, epoxy resins, phenolic resins, melamine resins, acrylic resins, cyanate resins or combinations thereof.

In some embodiments, the adhesive is an epoxy resin selected from the group consisting of: bisphenol A epoxy resins; bisphenol F epoxy

resins; bisphenol S epoxy resins; phenol novolac epoxy resins; cresol novolac epoxy resins; biphenyl epoxy resins; biphenyl aralkyl epoxy resins; aralkyl epoxy resins; dicyclopentadiene epoxy resins; multifunctional epoxy resins; naphthalene epoxy resins; phosphorus containing epoxy resins; rubber modified epoxy resins, and mixtures thereof.

In some embodiments, the adhesive epoxy resin contains a hardener and, optionally, further contains additional components, such as, an elastomer reinforcing agent, curing accelerator, filler and flame retardant.

In some embodiments, the suitable hardeners include phenolic compounds selected from the group consisting of: novolac phenol resins; aralkyl phenol resins; biphenyl aralkyl phenol resins; multifunctional phenol resins; nitrogen-containing phenol resins; dicyclopentadiene phenol resins; and phosphorus-containing phenol resins.

In another embodiment, the hardener is an aromatic diamine compound selected from the group consisting of: diaminobiphenyl compounds, e.g., 4,4'-diaminobiphenyl and 4,4'-diamino-2,2'-dimethylbiphenyl; diaminodiphenylalkane compounds, e.g., 4,4'-diaminodiphenylmethane and 4,4'-diaminodiphenylethane; diaminodiphenyl ether compounds, e.g., 4,4'-diaminodiphenylether and di(4-amino-3-ethylphenyl)ether; diaminodiphenyl thioether compounds, e.g., 4,4'-diaminodiphenyl thioether and di(4-amino-3-propylphenyl)thioether; diaminodiphenyl sulfone compounds, e.g., 4,4'-diaminodiphenyl sulfone and di(4-amino-3-isopropylphenyl)sulfone; and phenylenediamines. In one embodiment, the hardener is an amine compound selected from the group consisting of: guanidines, e.g., dicyandiamide (DICY); and aliphatic diamines, e.g., ethylenediamine and diethylenediamine.

The coverlay of the present disclosure has a CTE that closely matches the underlying circuit, high temperature dimensional stability and good flex endurance. The sub-micron filler of the present disclosure in the

polyimides of the present disclosure provide the potential for higher performing lower cost coverlays.

The embodiments illustrated and described above are provided merely as examples of certain preferred embodiments of the present invention. Various changes and modifications can be made from the
5 embodiments presented herein by those skilled in the art without departure from the spirit and scope of the invention, as defined by the appended claims.

10

EXAMPLES

The invention will be further described in the following examples, which are not intended to limit the scope of the invention described in the claims.

In all examples, for calculations to convert to composition weight
15 percentages to equivalent volume percentages, densities of 4.2 g/cc for the acicular titanium dioxide, 2.75 g/cc for talc, 3.22 g/cc for SiC and 1.42 g/cc for the polyimide were used.

Examples 1-4 demonstrate that the sub-micron filler of the present
20 disclosure at 10 volume percent or higher significantly increase storage modulus and lower CTE when compared to unfilled Comparative Example 1, while maintaining adequate elongation to break.

Example 1

25 15 vol % (34.3 wt %) acicular TiO₂ in PMDA//ODA.

25.0 grams of acicular TiO₂ (FTL-110, Ishihara Corporation, USA) was combined with 141.11 grams of anhydrous DMAC. This slurry was mixed at high shear for approximately 10 to 15 minutes using Silverson Model L4RT high-shear mixer (Silverson Machines, LTD, Chesham
30 Baucks, England) equipped with a square-hole, high-shear screen (with a blade speed of approximately 4000 rpm).

In a round bottom flask, 74.1 grams of the slurry containing acicular TiO₂ was mixed with 116.94 grams of PMDA//ODA prepolymer (20 wt %

solution in anhydrous DMAC), and the resulting mixture was stirred for approximately 24 hours. During this operation, a gentle nitrogen gas purge was used in the round bottom flask.

After stirring for approximately 24 hours, this material was filtered
5 through 45 micron filter media (Millipore, 45 micron polypropylene screen, PP4504700).

In a separate container, a 6 wt % solution of pyromellitic anhydride (PMDA) was prepared by combining 9.00 g of PMDA (Aldrich 412287, Allentown, PA) and 15 ml of DMAC.

10 The PMDA solution was slowly added to the prepolymer slurry to achieve a final viscosity of 1090 poise. The formulation was stored overnight at 0°C to allow it to degas.

The formulation was cast using a 25 mil doctor blade onto a surface of a glass plate to form a 3" x 4" film. The cast film and the glass plate is
15 then soaked in a solution containing 110 ml of 3-picoline (beta picoline, Aldrich, 242845) and 110 ml of acetic anhydride (Aldrich, 98%, P42053).

The film was subsequently lifted off of the glass surface, and mounted on a 3" x 4" pin frame. The mounted film was placed in a furnace (Thermolyne, F6000 box furnace). The furnace was purged with nitrogen
20 and heated according to the following temperature protocol:

40°C to 125°C (ramp at 4°C /min)
125°C to 125°C (soak 30 min)
125°C to 250°C (ramp at 4°C /min)
250°C (soak 30 min)
25 250°C to 400°C (ramp at 5°C /min)
400°C (soak 20 min)

The coefficient of thermal expansion was measured by thermomechanical analysis (TMA). A TA Instrument model 2940 was
30 used in tension mode. The instrument was purged with N₂ gas at 30-50 ml/min. A mechanical cooler was also used, which allowed temperature of the instrument to rapidly cool down between heating cycles. The film was cut to a 2.0 mm width and 6-9 mm length (in MD or casting direction). The

film was clamped lengthwise to a length of 7.5 -9.0 mm. A preload tension was set for 5 grams of force. The film was then subjected to heating from 0°C to 400°C at 10°C/min rate, held at 400°C for 3 minutes, and cooled back down to 0°C. A second heating cycle to 400°C was performed in the same way. The calculations of thermal expansion coefficient in the unit of $\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$ (or $\text{pp}/^{\circ}\text{C}$) from 60°C to 400°C were reported for the casting direction (MD) for the second heating cycle.

Storage modulus (E') was measured by a Dynamic Mechanical Analysis (DMA) instrument was used to characterize the mechanical behavior of the film. The DMA operation was based on the viscoelastic response of polymers subjected to a small oscillatory strain (e.g., 10 μm) as a function of temperature and time (TA Instruments, New Castle, DE, USA, DMA 2980). The films were placed under tension in a multifrequency-strain mode. A finite size of rectangular specimen was clamped between stationary jaws and movable jaws. The films were 6-6.4 mm in width, 0.03-0.05 mm thick and 10 mm in length. The MD direction was used, and the film was fastened with 3 in-lb torque force. The static force in the length direction was 0.05 N with autotension of 125%. The film was heated at frequency of 1 Hz from 0° to 500°C at a rate of 3°C/min. The storage modulus at 25°C was measured to be 5757 MPa.

Tensile properties (including % elongation at break) of the films were measured on an Instron model 3345 instrument. Crosshead gap (sample test length) was 1 inch (2.54 centimeters) and width was 0.5 inch (1.27 centimeters). Crosshead speed was 1 inch (2.54 centimeters)/min.

Results are shown in Table 1.

Example 2

10 vol % (24.70 wt %) acicular TiO_2 (FTL-110) in PMDA//ODA.

The same procedure as described in Example 1 was followed, with the following exceptions. 54.24 grams of the slurry containing acicular TiO_2 (FTL-110, 15 wt % in DMAC) was mixed with 136.15 grams of PMDA//ODA prepolymer (20 wt % in DMAC).

The material was finished with the PMDA solution to a viscosity of 99 poise.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

5 Example 3

20 vol % (42.5 wt %) acicular TiO₂ (FTL-110) in PMDA//ODA.

The same procedure as described in Example 1 was followed, with the following exceptions. 57.7 grams of the slurry containing acicular TiO₂ (FTL-110, 15 wt % in DMAC, high shear mixed) was combined with 63.3
10 grams of PMDA//ODA prepolymer (20.6 wt % in DMAC).

The material was finished with the PMDA solution to a viscosity of 1380 poise.

CTE, E' and % elongation at break were measured as in Example 1.

15 Results are shown in Table 1.

Example 4

10 vol % SiC fibers (20.1 wt %) in PMDA//ODA.

The same procedure as described in Example 1 was followed, except for the following differences. 24.75 grams of SiC fibers (Silar® Silicon Carbide whiskers, beta form, Advanced Composites Materials, Greer, SC, USA) was combined with 140.25 grams of anhydrous DMAC. The slurry was blended under high shear conditions, as described in Example 1.

25 45.62 grams of this slurry was combined with 144.44 grams of PMDA//ODA prepolymer (20.6 wt % in DMAC).

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

30

Comparative Example 1

Unfilled PMDA//ODA.

The same procedure as described in Example 1 was followed, with the following exceptions. The slurry containing the inorganic particles was not added to the PDMA//ODA prepolymer (prepolymer is 20 wt % in DMAC).

5 The material was finished with the PMDA solution to a viscosity of 890 poise.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

10

Comparative Examples 2-5 demonstrate the sub-micron filler of the present disclosure present below 10 volume percent does not produce a significant increase in storage modulus (especially storage moduli at 500°C) or decrease CTE (relatively minor improvement in storage modulus and CTE).

15

Comparative Example 2

2.5 vol % (7 wt %) acicular TiO₂ in PMDA//ODA.

A procedure similar to that described in Example 1 was used, except for the following differences. 24.08 grams of acicular TiO₂ (FTL-110, Ishihara Corporation, USA) was combined with 135.92 grams of anhydrous DMAC, and the slurry mixed at high shear.

10.1 grams of the slurry containing acicular TiO₂ was mixed with 109.9 grams of PMDA//ODA prepolymer.

25 CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

Comparative Example 3

30 5 vol % (13.5 wt %) acicular TiO₂ in PMDA//ODA.

A procedure similar to that described in Example 1 was used, except for the following differences. 24.08 grams of acicular TiO₂

(FTL-110, Ishihara Corporation, USA) was combined with 135.92 grams of anhydrous DMAC, and the slurry mixed at high shear.

19.1 grams of the slurry containing acicular TiO₂ was mixed with 100.9 grams of PMDA//ODA prepolymer.

5 CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

Comparative Example 4

10 6.5 vol % (17.1wt %) acicular TiO₂ in PMDA//ODA.

A procedure similar to that described in Example 1 was used, except for the following differences. 24.08 grams of acicular TiO₂ (FTL-110, Ishihara Corporation, USA) was combined with 135.92 grams of anhydrous DMAC, and the slurry mixed at high shear.

15 23.96 grams of the slurry containing acicular TiO₂ was mixed with 96.1 grams of PMDA//ODA prepolymer.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

20

Comparative Example 5

8.5 vol % (21.6wt %) acicular TiO₂ in PMDA//ODA.

A procedure similar to that described in Example 1 was used, except for the following differences.

25 24.08 grams of acicular TiO₂ (FTL-110, Ishihara Corporation, USA) was combined with 135.92 grams of anhydrous DMAC, and the slurry mixed at high shear.

30.0 grams of the slurry containing acicular TiO₂ was mixed with 90.0 grams of PMDA//ODA prepolymer.

30 CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

Comparative Example 6

15 vol. % (34.3 wt %) less than 3:1 aspect ratio TiO₂ in PMDA//ODA.

Comparative Example 6 demonstrates that filler having an aspect ratio less than 3:1 produces a film with lower storage modulus and higher CTE compared to Example 1 which has sub-micron filler with an aspect ratio of at least 3:1 at 15 volume percent. The film was brittle on the edges, and would not be viable in a commercial manufacturing process.

The same procedure as described in Example 1 was followed, with the following exceptions. 33.84 grams of the slurry containing DuPont Light Stabilized Titania, 210 (Du Pont, Wilmington, Delaware, 25 wt % in DMAC, high shear mixed) was combined with 86.2 grams of PMDA//ODA prepolymer (20.6 wt % in DMAC).

The material was finished with the PMDA solution to a viscosity of 1100 poise.

DuPont Titania 210 is a fine white powder with a distribution of particles centered in the range of 130-140 nm on a weight basis. The particles are roughly spherical.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

Comparative Example 7

Unfilled BPDA//PPD.

The same procedure as described for Comparative Example 8 was followed, except that acicular TiO₂ was not added to the formulation.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

Comparative Examples 8-9 demonstrate that the sub-micron filler of the present disclosure does not behave predictably in all polyimides. In the case of a BPDA//PPD system, CTE dramatically increases (greater

than a factor of 2) with approximately 15 vol % of acicular of TiO₂ is introduced.

Comparative Example 8

- 5 14.64 vol % (33.7 wt %) acicular TiO₂ (FTL-110) in BPDA//PPD.
CTE increased with the introduction of acicular TiO₂.

BPDA//PPD prepolymer (69.3 g of a 17.5 wt % solution in anhydrous DMAC) was combined with 5.62 g of acicular TiO₂ (FTL-110, 10 Ishihara Corporation, USA) and the resulting slurry was stirred for 24 hours. In a separate container, a 6 wt % solution of pyromellitic anhydride (PMDA) was prepared by combining 0.9 g of PMDA (Aldrich 412287, Allentown, PA) and 15 ml of DMAC.

The PMDA solution was slowly added to the prepolymer slurry to 15 achieve a final viscosity of 653 poise. The formulation was stored overnight at 0°C to allow it to degas.

The formulation was cast using a 25 mil doctor blade onto a surface of a glass plate to form a 3" x 4" film. The glass was pretreated with a release agent to facilitate removal of the film from the glass surface. The 20 film was allowed to dry on a hot plate at 80°C for 20 minutes. The film was subsequently lifted off the surface, and mounted on a 3" x 4" pin frame.

After further drying at room temperature under vacuum for 12 hours, the mounted film was placed in a furnace (Thermolyne, F6000 box 25 furnace). The furnace was purged with nitrogen and heated according to the following temperature protocol:

- 125°C (30 min)
- 125°C to 350°C (ramp at 4°C /min)
- 350°C (30 min)
- 30 • 350°C to 450°C (ramp at 5°C /min)
- 450°C (20 min)
- 450°C to 40°C (cooling at 8°C /min)

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

5 Comparative Example 9

14.64 vol % acicular TiO₂ (FTL-110) in BPDA//PPD.

The elongation to break is very low. The film is too brittle to be manufacturable.

The same procedure as described in Example 1 was used, except
 10 for the following differences. 33.99 grams of acicular TiO₂ (FTL-110, Ishihara Corporation, USA) was combined with 191.9 grams of anhydrous DMAC. This slurry was mixed at high shear for approximately 10 to 15 minutes using Silverson Model L4RT high-shear mixer (Silverson Machines, LTD, Chesham Baucks, England) equipped with a square-hole,
 15 high-shear screen (with a blade speed of approximately 4000 rpm).

129.25 g of BPDA//PPD prepolymer (17.5 wt % solution in anhydrous DMAC) was combined with 69.335 grams of the slurry containing acicular TiO₂. The resulting slurry was stirred for 24 hours. In a separate container, a 6 wt % solution of pyromellitic anhydride (PMDA)
 20 was prepared by combining 0.9 g of PMDA (Aldrich 412287, Allentown, PA) and 15 ml of DMAC.

The PMDA solution was slowly added to the prepolymer slurry to achieve a final viscosity of 998 poise.

After chemical imidization the film was lifted off of the glass surface,
 25 and mounted on a 3" x 4" pin frame. The mounted film was placed in a furnace (Thermolyne, F6000 box furnace). The furnace was purged with nitrogen and heated according to the following temperature protocol:

	125°C	(30 min)
	125°C to 350°C	(ramp at 4°C /min)
30	350°C	(30 min)
	350°C to 450°C	(ramp at 5°C /min)
	450°C	(20 min)
	450°C to 40°C	(cooling at 8°C /min)

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

5 Comparative Example 10

Unfilled PMDA//ODA.

Three 180 g portions of a prepolymer of PMDA and ODA (prepared in DMAC at about 20.6%, approximately 50 poise viscosity) were diluted to 18% polymer solids via the addition of 26 g of DMAC to give three 206 g portions of diluted polymers. One of these three diluted prepolymer samples was reacted ("finished") to a viscosity of about 2100 poise (Brookfield DV-II+ viscometer with a #LV5 spindle) by stepwise additions of a 6 wt % PMDA solution in DMAC with thorough mixing to increase the molecular weight (hereafter referred to as "finished polymer"). After pressure filtering the solution through a polypropylene screen filter disk (45 micron), the solution was degassed under vacuum to remove air bubbles and then this solution was cast onto a letter size sheet of clear polyester film (approximately 3 mil thick). The polyamic acid coating on the polyester sheet was subsequently immersed in a bath containing a 1/1 v/v mixture of acetic anhydride and 3-picoline. After about 2 minutes, once the partially imidized coating began to separate from the polyester sheet, it was removed from the bath and pinned on a approximately 8"x 8" pin frame and allow to stand at room temperature in a lab hood for about 10-20 min. Next, the film on the pin frame was placed in a nitrogen purged oven and after purging at about 40°C for 30 minutes, this oven was ramped to 320°C over 70 minutes, held there for 30 minutes, then ramped to 450°C over about 16 minutes, and held there for 4 minutes, in order to cure to polyimide. After cooling, the resulting 2.4 mil (61 micron) film was removed from the oven and pin frame.

30 Storage modulus (E') by Dynamic Mechanical Analysis (TA Instruments, DMA-2980, 5°C/min) was measured by heating from room temperature to 500°C at 5°C/min.

Coefficient of thermal expansion (CTE) by Thermal Mechanical Analysis (TA Instruments, TMA-2940, heat 10°C/min, up to 460°C, then cool and reheat to 500°C) was evaluated between 50-350°C on the reheat.

5 % Tensile Elongation (Instron model 3345 tensile tester) – 0.5 in specimen width, 1 inch (2.54 centimeters) gauge length, 1 inch (2.54 centimeters)/min crosshead speed.

Results are shown in Table 1.

10 Comparative Example 11

5.4 vol % (10 wt %) Talc in PMDA//ODA.

Comparative Example 11 demonstrates talc below about 5.5 volume percent does not behave predictably.

In a similar manner to comparative Example 10, a portion of a
15 prepolymer of PMDA and ODA (prepared in DMAC at about 20.6%, approximately 50 poise viscosity) was diluted to 18% polymer solids via the addition of DMAC. Then, the prepolymer was blended with SF310 talc for several minutes in a Thinky ARE-250 centrifugal mixer to yield a dispersion of the filler in the PAA solution, to achieve about a 10 wt %
20 loading in the PI film. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. A 1 mil (25 micron) film was produced.

CTE, E' and % elongation at break were measured as in comparative Example 10.

25 Results are shown in Table 1.

Examples 5-9 demonstrate talc above about 5.5 volume percent significantly increase storage modulus and lower CTE while maintaining adequate elongation to break.

30

Example 5

14.0 vol % (24 wt %) Talc in PMDA//ODA.

The same procedure as described in Example 1 was followed, with the following exceptions. 25 grams of talc (Flexalc 610, Kish Company, Inc., Mentor, OH) was mixed, at high shear, with 141 grams of anhydrous DMAC.

5 55.9 grams of this slurry was mixed with 134.7 grams of PMDA//ODA prepolymer.

CTE, E' and % elongation at break were measured as in Example 1.

Results are shown in Table 1.

10

Example 6

18 vol % (30 wt %) Talc in PMDA//ODA.

In a similar manner to comparative Example 11, the second of the 206 g portions of the diluted prepolymer from comparative Example 10 was blended with 14.77 g of Flexalc 610 (Lot M1085, Kish Co., Mentor, OH). Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 3.2 mil (81 micron) film was produced.

15 CTE, E' and % elongation at break were measured as in comparative Example 10.

Results are shown in Table 1.

Example 7

18.1 vol % (30 wt %) Talc in PMDA//ODA.

25 In a similar manner to Comparative Example 11, the third of the 206 g portions of the diluted prepolymer from comparative Example 10 was blended with 14.77 g of SF310 talc (Kish Co., Mentor, OH). Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 3.2 mil (81 micron) film was produced.

30 CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

Example 8

34 vol % (50 wt %) Talc in PMDA//ODA.

In a similar manner to comparative Example 11, the PMDA//ODA
5 prepolymer was blended with SF310 talc to achieve about a 50 wt %
loading in the PI film. Finishing, filtration, casting and curing was similar to
as described in comparative Example 10. Filler loading was approximately
50 wt % in the polyimide film. A 1.8 mil (46 micron) film was produced.

CTE, E' and % elongation at break were measured as in
10 comparative Example 10.

Results are shown in Table 1.

Example 9

43.6 vol % (60 wt %) Talc in PMDA//ODA.

In a similar manner to comparative Example 11, the PMDA//ODA
15 prepolymer was blended with SF310 talc to achieve about a 60 wt %
loading in the PI film. Finishing, filtration, casting and curing was similar to
as described in Comparative Example 10. A 1.3 mil (33 micron) film was
produced.

CTE, E' and % elongation at break were measured as in
20 Comparative Example 10.

Results are shown in Table 1.

Examples 10-11 demonstrate sub-micron fillers of the present
25 disclosure in polyimide copolymers above 10 volume percent significantly
increases storage modulus and lowers CTE when compared to unfilled
copolymer in comparative Example 13.

Example 10

18.1 vol % (30 wt %) Talc in random copolymer of PMDA//ODA/PPD
30 100//70/30.

In a similar manner to comparative Example 11, a 186.87 g portion
of the prepolymer from comparative Example 13 was blended with 13.13 g
of Flexalco 610 (Lot M6734, Kish Co., Mentor, OH). Finishing, filtration,

casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 2.2 mil (56 micron) film was produced.

CTE, E' and % elongation at break were measured as in
5 Comparative Example 10.

Results are shown in Table 1.

Example 11

12.6 vol % (30 wt %) acicular TiO₂ in random copolymer of
10 PMDA//ODA/PPD 100//70/30.

In a similar manner to Comparative Example 11, a 173 g portion of the prepolymer from Comparative Example 13 was blended with 27 g of a milled/dispersed 45 wt% slurry of acicular TiO₂ (FTL-110 powder from Ishihara Corp. (USA)) in DMAC. Finishing, filtration, casting and curing
15 was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 1.1 mil (28 micron) film was produced.

CTE, E' and % elongation at break were measured as in
Comparative Example 10.

20 Results are shown in Table 1.

Comparative Example 12

Unfilled random copolymer of PMDA//ODA/PPD 100//70/30.

In a 1.5 liter beaker inside a nitrogen purged glove box, 15.118 g of
25 PPD (0.1398 moles) and 65.318 g (0.3262 moles) ODA were added to 779.2 g of DMAC well agitated with a mechanical stirrer. After brief mixing at room temperature, 99.612 g (0.4567 moles) of PMDA was slowly added to maintain the temperature below 40°C, followed by 41.0 g DMAC and the reaction was allowed to proceed for about 2 hours. The resulting
30 prepolymer solution (98% overall stoichiometry of dianhydride to diamine, 18% polymer solids), was decanted into a bottle and stored in a freezer until use. A portion of this prepolymer was finished similarly as in Example

A, filtered, and then a film was cast and cured similarly to Comparative Example 10. A 1.4 mil (36 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

5 Results are shown in Table 1.

Examples 12 and 13 demonstrate that a mixture of sub-micron fillers of the present disclosure significantly increase storage modulus and lower CTE when compared to unfilled polyimide in comparative Example
10 10.

Example 12

10 wt % talc, 20 wt % acicular TiO₂ in polymer of PMDA//ODA.

A 168.21 g portion of a prepolymer of PMDA and ODA (prepared in
15 DMAC at about 20.6%, approximately 50 poise viscosity) was blended together with 4.60 g SF310 talc and 20.46 g FTL-110 TiO₂ (45% slurry as described in Example 11 to achieve 10 wt% and 20 wt% loading respectively of the sub-micron fillers in the PI film (30 wt % total). Finishing, filtration, casting and curing was similar to as described in
20 Comparative Example 10. A 1.0 mil (25 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

25 Example 13

20 wt % talc, 10 wt % acicular TiO₂ in polymer of PMDA//ODA.

In a similar manner to Example 12, a 173.13 portion of the PMDA//ODA prepolymer was blended together with 9.45 g SF310 talc and 10.50 g FTL-110 TiO₂ (45% slurry as described in Example 11) to achieve
30 20 wt % and 10 wt % loading respectively of the sub-micron fillers in the PI film (30 wt % total). Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. A 2.2 mil (56 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

5 Examples 14 and 15 demonstrate a TiO₂ sub-micron filler of the present disclosure does not behave in the same manner in all polyimides in regards to CTE.

Example 14

10 11.7 vol % acicular TiO₂ (28.23 wt %) in block copolymer of PMDA//ODA/PPD 100//80/20.

High aspect ratio TiO₂ in the block copolymer of Example 14 significantly increases storage modulus while largely maintaining CTE compared to unfilled block copolymer of Comparative Example 13.

15

A similar procedure as described in Example 1 was used, except for the following differences. To prepare the prepolymer, 1.36 grams of PPD was combined with 110.0 grams of anhydrous DMAC and stirred, with gentle heating at 40°C for approximately 20 minutes. 2.71 grams of
20 PMDA was then added to this mixture to create the first block, which was stirred with gentle heating (35-40°C) for approximately 2.5 hours. The mixture was allowed to cool to room temperature.

To this formulation, 10.10 grams of ODA was added and allowed to dissolve in to the formulation for about 5 minutes. An ice water bath was
25 then used to control the temperature during the subsequent PMDA addition. 10.9 g PMDA was slowly added to this mixture. An addition 15 grams of DMAC was added to the formulation and the reaction was allowed to stir with gentle heat (30-35°C) for 90 minutes. The mixture was allowed to stir at room temperature for approximately 18 hours.

30 In a separate container, 20.88 grams of acicular TiO₂ (FTL-11) was combined with 25.52 g of anhydrous DMAC and 0.426 g of Solplus D540 (Lubrizol) and milled for 24 hours in a jar mill using 8 mm spherical milling media.

14.2 gram of the slurry containing TiO₂ was mixed with 105.8 grams of the prepolymer formulation described above.

A modified heating procedure was used, as shown below:

- 5 40°C to 125°C (ramp at 4°C /min)
 125°C (soak 30 min)
 125°C to 350°C (ramp at 4°C /min)
 350°C to 350°C (soak 30 min)
 350°C to 450°C (ramp at 5°C /min)
10 450°C (soak 20 min)
 CTE, E' and % elongation at break were measured as in Example
 1.

Results are shown in Table 1.

15 Example 15

17.5 vol % acicular TiO₂ (38.5 wt %) in block copolymer of PMDA//ODA/PPD 100//80/20.

High aspect ratio TiO₂ in the block copolymer of 15 significantly increases storage modulus while slightly decreasing CTE in the transverse
20 direction compared to unfilled block copolymer of comparative Example 13.

A similar procedure as described in Example 1 was used, except for the following differences. To prepare the prepolymer, 1.36 grams of PPD was combined with 113.0 grams of anhydrous DMAC and stirred,
25 with gentle heating at 40°C for approximately 20 minutes. 2.71 grams of PMDA was then added to this mixture to create the first block, which was stirred with gentle heating (35-40°C) for approximately 2.5 hours. The mixture was allowed to cool to room temperature.

To this formulation, 10.10 grams of ODA was added and allowed to
30 dissolve in to the formulation for about 5 minutes. An ice water bath was then used to control the temperature during the subsequent PMDA addition. 10.9 g PMDA was slowly added to this mixture. An additional 12 grams of DMAC was added to the formulation and the reaction was

allowed to stir with gentle heat (30-35 degrees) for 90 minutes. The mixture was allowed to stir at room temperature for approximately 18 hours.

In a separate container, 20.88 grams of acicular TiO₂ (FTL-11) was combined with 25.52 g of anhydrous DMAC and 0.426 g of Solplus D540 (Lubrizol) and milled for 24 hours in a 4" (internal diameter) nylon jar mill using 8 mm spherical milling media, turning at 80 rpm.

15.34 gram of the slurry containing TiO₂ was mixed with 72.0 grams of the prepolymer formulation described above.

10

A modified heating procedure was used, as shown below:

40°C to 125°C (ramp at 4°C /min)

125°C (soak 30 min)

125°C to 350°C (ramp at 4°C /min)

15 350°C to 350°C (soak 30 min)

350°C to 450°C (ramp at 5°C /min)

450°C (soak 20 min)

CTE, E' and % elongation at break were measured as in Example

1.

20

Results are shown in Table 1.

Comparative Example 13

Unfilled block copolymer of PMDA//ODA/PPD 100//80/20.

The same procedure was used as described in Example 15 was used, except that the acicular TiO₂ slurry was not added to the formulation. The final viscosity of the formulation was 1000-1200 poise.

CTE, E' and % elongation at break were measured as in Example

1.

Results are shown in Table 1.

30

Example 16

12.6 vol % acicular TiO₂ (30wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

Example 16 demonstrates acicular TiO₂ sub-micron filler of the present disclosure does not behave in the same manner in all polyimides in regards to CTE. CTE increases compared to unfilled block copolymer in Comparative Example 14 but still remains in a desirable range.

5

In a similar manner to Comparative Example 11, a 173 g portion of the prepolymer from comparative Example 14 was blended with 27 g of a milled/dispersed 45 wt % slurry of acicular TiO₂ (FTL-110 powder from Ishihara Corp. (USA)) in DMAC. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 3.0 mil (76 micron) film was produced.

10

CTE, E' and % elongation at break were measured as in Comparative Example 10.

15

Results are shown in Table 1.

Comparative Example 14

Unfilled block copolymer of PMDA//ODA/PPD 100//70/30.

20

In a 1.5 liter beaker inside a nitrogen purged glove box, 15.115 g of PPD were added to 396.7 g of DMAC well agitated with a mechanical stirrer. After brief mixing at room temperature (some but not all PPD had dissolved), 28.962 g of PMDA was slowly added to maintain the temperature below 40°C. The monomers dissolved and reacted and the polyamic acid (PAA) solution was allowed to stir for 1 hr. Afterwards, the solution was diluted with 382.3 g of DMAC and then 65.304 g ODA was added. This solution was stirred for 30 min and the ODA dissolved into the PAA solution. Subsequently, 70.627 g of PMDA was slowly added, followed by 41.0 g DMAC and the reaction was allowed to proceed for about 2 hours. The resulting prepolymer solution (98% overall stoichiometry of dianhydride to diamine, 18% polymer solids), was decanted into a bottle and stored in a freezer until use. A 180 g portion of this prepolymer was finished as in comparative Example 10 to about 2200

25

30

poise, filtered, and then a film was cast and cured similarly to Comparative Example 10. Properties of the resulting 2.2 mil (56 micron) film CTE, E' and % elongation at break were measured as in Comparative Example 10.

5 Results are shown in Table 1.

Examples 17-20 demonstrate block copolymer with talc above about 5.5 volume percent significantly increase storage modulus and maintain CTE while maintaining adequate elongation to break.

10

Example 17

18.1 vol % Talc (30 wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

15 A 186.87 g portion of the prepolymer prepared in Comparative Example 14 was blended with 13.13 g of SF-310 talc (Lot M685, Kish Co., Mentor, OH) in a similar manner to Comparative Example 11. This filler containing PAA solution was finished similarly as in Comparative Example 10 to yield a viscosity of ca. 2000 poise. The solution was pressured filtered through a 45 micron polypropylene screen and degassed under
20 vacuum to remove air bubbles. A film was cast and cured similarly comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 2.6 mil (66 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

25 Results are shown in Table 1.

Example 18

18.1 vol % Talc (30wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

In a similar manner to comparative Example 11, a 186.87 g portion of the prepolymer from comparative Example 14 was blended with 13.13 g of Flexcalc 610 (Lot M1085, Kish Co., Mentor, OH). Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt% in the polyimide film. A 2.9 mil (74 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

Example 19

25.6 vol % Talc (40wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

In a similar manner to comparative Example 15, the PMDA//ODA/PPD 100//70/30 block prepolymer was blended with SF310 talc to achieve about a 40 wt % loading in the PI film. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. A 1.8 mil (46 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

Example 20

34 vol % Talc (50 wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

In a similar manner to Comparative Example 14, a block prepolymer was prepared with a 70/30 ratio of ODA to PPD. Then in a similar manner to Comparative Example 11, a 171.75 g portion of this prepolymer was blended with 28.255 g SF310 talc to achieve about a 50 wt % loading in the PI film. Finishing, filtration, casting and curing was

similar to as described in Comparative Example 10. A 1.5 mil (38 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

5 Results are shown in Table 1.

Comparative Example 15

5.4 vol % Talc (10 wt %) Filled block copolymer of PMDA//ODA/PPD 100//70/30.

10 Comparative Example 15 demonstrates talc below about 5.5 volume percent does not significantly increase storage modulus.

In a similar manner to Comparative Example 14, a block prepolymer was prepared with a 70/30 ratio of ODA to PPD. Then in a similar manner to Comparative Example 11, a 187.16 g portion of this prepolymer was blended with 3.48 g SF310 talc to achieve about a 10 wt % loading in the PI film. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. A 1.7 mil (43 micron) film was produced.

20 CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

The Examples 21-24 illustrate the ability to include additional co-monomers in the compositions of the present invention and still achieve desirable properties.

Example 21

18.1 vol % (30 wt %) Talc Filled block copolymer of PMDA/BPDA//ODA/PPD 95/5//70/30.

In a similar manner to Comparative Example 14, a prepolymer was produced from 14.988 g PPD and 28.720 g PMDA in 393.4 g DMAC, followed by dilution with 386.8 g DMAC, then addition of 64.758 g ODA,

and then 6.796 g of BPDA (which was allowed to dissolve/react), then 64.998 g of PMDA, followed by 41.0 g DMAC. A 186.8 g portion of this prepolymer was blended with 13.17 g SF310 talc (Lot M685, Kish Co., Mentor, OH) similar to Comparative Example 11, finished as in
5 Comparative Example 10, filtered, and then a film was cast and cured similarly to Comparative Example 10. A 2.0 mil (51 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

10 Results are shown in Table 1.

Example 22

12.6 vol % (30 wt %) Acicular TiO₂ Filled Block Copolymer of PMDA/BPDA//ODA/PPD 95/5//70/30.

15 In a similar manner to Example 21, a 172.7 g portion of the prepolymer from Example 21 was blended with a 27.3 g portion of the TiO₂ slurry as described in Example 16. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. Filler loading was approximately 30 wt % in the polyimide film. A 2.2 mil (56
20 micron) film was produced.

CTE, E' and % elongation at break were measured as in Comparative Example 10.

Results are shown in Table 1.

25 Example 23

18.1 vol % (30 wt %) Talc Filled block copolymer of PMDA/BPDA//ODA/PPD 75/25//70/30.

In a similar manner to Comparative Example 14, a prepolymer was produced from 14.407 g PPD and 27.607 g PMDA in 378.1 g DMAC,
30 followed by dilution with 401 g DMAC, then addition of 62.249 g ODA, and then 32.666 g of BPDA (which was allowed to dissolve/react), then 43.106 g of PMDA, followed by 41.0 g DMAC. A 186.8 g portion of this prepolymer was blended with 13.17 g SF310 talc (Lot M685, Kish Co.,

Mentor, OH) similar to comparative Example 11, finished, cast and cured similarly to Comparative Example 10. A 1.7 mil (43 micron) film was produced.

CTE, E' and % elongation at break were measured as in
5 Comparative Example 10.

Results are shown in Table 1.

Example 24

12.6 vol % (30 wt %) Acicular TiO₂ Filled Block Copolymer of
10 PMDA/BPDA//ODA/PPD 75/25//70/30.

In a similar manner to Example 23, a 172.7 g portion of the prepolymer from Example 23 was blended with a 27.3 g portion of the TiO₂ slurry as described in Example 16. Finishing, filtration, casting and curing was similar to as described in Comparative Example 10. A 2.3 mil
15 (58 micron) film was produced.

CTE, E' and % elongation at break were measured as in
Comparative Example 10.

Results are shown in Table 1.

20 The following examples demonstrate the impact on properties of a particulate (less than 3:1 aspect ratio) vs. a high aspect ratio (greater than 3:1 aspect) ratio platelet filler on the properties of a polyimide film. The platelet filler results in advantageously higher modulus and lower CTE at equivalent weight loadings. (Note that although the average particle sizes
25 of these two fillers appear significantly different (platelet is significantly larger) via particle size analysis (Horiba LA-930 particle size analyzer), it is believed that the effect on properties is largely due to the filler shape, rather than any differences in average particle size).

30 Comparative Example 16

(40 wt %) less than 3:1 aspect ratio Al₂O₃ (particulate) in PMDA//ODA.

A portion of a polyamic acid prepolymer of PMDA and ODA (prepared in DMAC at about 20.6%, approximately 50 poise viscosity) was

blended with particulate alumina filler (Martoxid MZS-1, Albermarle Corporation) in a Silverson (model L4RT-A) high shear mixer. The amount of alumina was chosen so as to ultimately yield a final polyimide film with a 40 wt % loading of alumina in polyimide. The polyamic acid was then further reacted ("finished") to a viscosity of about 537 poise (Brookfield DV-II+ viscometer with a #LV5 spindle) by stepwise additions of a 6 wt % PMDA solution in DMAC with thorough mixing via a high torque mechanical mixer/stir blade. The polymer was subsequently cast onto a glass plate and heated to about 80°C until a tack free film was obtained. The film was carefully peeled from the glass and placed on a pin frame and placed in a circulating air oven and the temperature slowly ramped to 320°C and held there for 30 minute. Next, the film was removed from the 320°C oven and place in a 400°C air oven for 5 minutes. Afterwards, the polyimide film on the pin frame was removed from the oven and allowed to cool to room temperature. The film was then separated from the pin frame.

E' was measured as in Comparative Example 10. CTE was measured on the same instrument and at the same rate as Comparative Example 10 except that the sample was heated to 380°C, then cooled and reheated to 380°C) and evaluated between 50-350°C on the reheat.

Results are shown in Table 1.

Example 25

(40 wt %) greater than 3:1 aspect ratio Al₂O₃ (platy) in PMDA//ODA.

In a similar manner to Comparative Example 16, a portion of the PMDA//ODA prepolymer was blended with a platelet-shaped alumina ("Platyl" from Advanced Nanotechnology Limited, Australia) at the same loading level as the particular alumina from Comparative Example 16 and finished to a Brookfield viscosity of 502 poise). This filled polymer solution was cast and thermally cured as in Comparative Example 16.

E' was measured as in Comparative Example 10. CTE was measured on the same instrument and at the same rate as Comparative Example 16.

Results are shown in Table 1.

Note that not all of the activities described above in the general description or the examples are required, that a portion of a specific activity may not be required, and that further activities may be performed in addition to those described. Still further, the order in which each of the activities are listed are not necessarily the order in which they are performed. After reading this specification, skilled artisans will be capable of determining what activities can be used for their specific needs or desires.

In the foregoing specification, the invention has been described with reference to specific embodiments. However, one of ordinary skill in the art appreciates that various modifications and changes can be made without departing from the scope of the invention as set forth in the claims below. Accordingly, the specification is to be regarded in an illustrative rather than a restrictive sense and all such modifications are intended to be included within the scope of the invention.

Benefits, other advantages, and solutions to problems have been described above with regard to specific embodiments. However, the benefits, advantages, solutions to problems, and any element(s) that may cause any benefit, advantage, or solution to occur or become more pronounced are not to be construed as a critical, required, or essential feature or element of any or all the claims.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper values and lower values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

Table 1

	POLYMER (ODA/PPD ratio)	Filler	wt %	Equivalent vol %, using density of 1.42 g/cc for polymer, 4.2 g/cc for acicular TiO ₂ , 2.75 g/cc for talc, 3.22 g/cc for SiC	E' at 50 °C (unless otherwise noted) GPa	E' at 300°C, GPa	E' at 480°C GPa	CTE MD, ppm/C	CTE TD, ppm/C	% TENSILE ELONGATION to Break MD/TD
1	PMDA/ODA	Acicular TiO ₂	34.3	15.00	5.7 (25°C)	3.2	0.854 (500°C)	24.0	26.4	35.6 MD
2	PMDA/ODA	Acicular TiO ₂	24.7	10.00	6.2 (25°C)	3.5	0.875 (500°C)	24.6	32.4	
3	PMDA/ODA	Acicular TiO ₂	42.5	20.00	6.14 (25°C)	3.6	1.02 (500°C)	27.1	17.4	
4	PMDA/ODA	SiC fiber	20.1	10.00	5.3 (25°C)	2.7	0.27 (500°C)	22.0	31.2	35.8 MD
Comp.1	PMDA/ODA	None	0	0.00	3.5 (25°C)	1.8	0.4 (500°C)	38.4	39.6	
Comp. 2	PMDA/ODA	acicular TiO ₂	7	2.50	3.9 (25°C)	2.1	0.51 (500°C)	38.0	38.6	
Comp. 3	PMDA/ODA	acicular TiO ₂	13.5	5.00	4.4 (25°C)	2.3	0.55 (500°C)	31.0	36.8	

Comp. 4	PMDA/ODA	acicular TiO ₂	17.1	6.50	4.4 (25°C)	2.4	0.61 (500°C)	30.0	33.8	
Comp. 5	PMDA/ODA	acicular TiO ₂	21.6	8.50	4.3 (25°C)	2.2	0.51 (500°C)	32.9	34.1	
Comp 6	PMDA/ODA	Spherical TiO ₂	34.3	15.00	4.42 (25°C)	2.2	0.48 (500°C)	37.7	43.5	
Comp. 7	BPDA/PPD	None	0	0.00				10.8		
Comp. 8	BPDA/PPD	acicular TiO ₂	33.7	14.64				23.0		
Comp. 9	BPDA/PPD all rigid rod	acicular TiO ₂	33.7	14.64						6
Comp. 10	PMDA/ODA	None	0	0.00	2.9		0.29	43.0	42.0	
Comp. 11	PMDA/ODA	Talc	10	5.42	3.0		0.21	29.0	23.0	126/136
5	PMDA/ODA	Talc	24	14.02	5.7 (25°C)			25.4		
6	PMDA/ODA	Talc	30	18.08	5.8		0.78	24.0	23.0	178/181
7	PMDA/ODA	Talc	30	18.08	5.4		0.86	21.0	19.0	171/148
8	PMDA/ODA	Talc	50	34.00	8.9		1.20	11.0	13.0	56/73
9	PMDA/ODA	Talc	60	43.60	11.1		1.96	8.0	9.0	42/56

10	PMDA/ODA/PPD Random (70/30)	Talc	30	18.08	7.1		1.17	13.0	17.0	63/41
11	PMDA/ODA/PPD Random (70/30)	acicular TiO ₂	30	12.64	6.3		0.87	18.0	25.0	27/45
Comp. 12	PMDA/ODA/PPD Random (70/30)	None	0	0.00	4.5		0.45	23.0	25.0	122/123
12	PMDA/ODA	Talc 10 wt% TiO ₂ , 20 wt%			7.3		0.94	21.0	29.0	69/72
13	PMDA/ODA	Talc 20 wt% TiO ₂ , 10 wt%			5.9		0.94	19.0	21.0	76/78
14	PMDA/ODA/PPD 80/20	acicular TiO ₂	28.23	11.74	6.8 (25°C)	4.0	1.5 (500°C)	23.0	21.0	
15	PMDA/ODA/PPD 80/20	acicular TiO ₂	38.5	17.50	7.1 (25°C)	4.1	1.3 (500°C)	20.0	17.5	
Comp. 13	PMDA/ODA/PPD 80/20	None	0	0.00	3.5	2.0	1.2 (500°C)	23.0	24.0	
16	PMDA/ODA/PPD 70/30	acicular TiO ₂	30	12.64	7.5		1.22	15.0	14.0	41/53
Comp. 14	PMDA/ODA/PPD 70/30	None	0	0.00	5.2		0.70	7.0	9.0	107/124
17	PMDA/ODA/PPD 70/30	Talc	30	18.08	6.9		1.24	9.0	9.0	84/69
18	PMDA/ODA/PPD 70/30	Talc	30	18.08	7.4		1.34	8.0	13.0	62/54
19	PMDA/ODA/PPD 70/30	Talc	40	25.62	9.5		1.80	10.0	9.0	58/52
20	PMDA/ODA/PPD 70/30	Talc	50	34.00	11.1		2.60	8.0	7.0	31/41

Comp. 15	PMDA/ODA/PPD 70/30	Talc	10	5.42	5.4		0.72	9.0	4.0	60/66
21	PMDA/BPDA/ODA/PPD 95/5//70/30	Talc	30	18.08	9.7 (25°C)		1.42 (498°C)	6.0	10.0	60/80
22	PMDA/BPDA/ODA/PPD 95/5//70/30	acicular TiO ₂	30	12.64	8.3 (25°C)		1.26 (498°C)	11.0	17.0	40/56
23	PMDA/BPDA/ODA/PPD 75/25//70/30	Talc	30	18.08	10.9 (25°C)		0.88 (498°C)	8.0	11.0	51/38
24	PMDA/BPDA/ODA/PPD 75/25//70/30	acicular TiO ₂	30	12.64	9 (25°C)		0.61 (498°C)	11.0	20.0	32/68
Comp. 16	PMDA/ODA	particle Al ₂ O ₃	40		4.1		0.28	52.0		
25	PMDA/ODA	platy Al ₂ O ₃	40		6.6		1.10	20.0		

CLAIMS

What is claimed is:

- 5 1. A coverlay composition comprising:
- A) a polyimide film comprising:
- a) a polyimide derived from:
- 10 i) at least one aromatic dianhydride
 component selected from the group
 consisting of rigid rod dianhydride, non-
 rigid rod dianhydride and combinations
 thereof, and
- 15 ii) at least one aromatic diamine
 component selected from the group
 consisting of rigid rod diamine, non-rigid
 rod diamine and combinations thereof;
- 20 wherein the mole ratio of dianhydride to
 diamine is 48-52:52-48 and the ratio of
 X:Y is 20-80:80-20 where X is the mole
 percent of rigid rod dianhydride and rigid
 rod diamine, and Y is the mole percent
- 25 of non-rigid rod dianhydride and non-
 rigid rod diamine based upon the total
 dianhydride component and total
 diamine component of the polyimide;
 and
- 30 b) a sub-micron filler:

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- i) being less than 550 nanometers (as a numerical average) in at least one dimension;
 - ii) having an aspect ratio greater than 3:1;
 - iii) being less than the polyimide film thickness in all dimensions;
 - iv) being present in an amount from 10 to 45 volume percent of the polyimide film;

10 wherein the polyimide film has a thickness from 5 to 150 microns; and

B) an adhesive layer selected from polyimide resins, epoxy resins, phenolic resins, melamine resins, acrylic resins, cyanate
15 resins or combinations thereof.

2. The coverlay composition in accordance with Claim 1, wherein the sub-micron filler is less than 400 nanometers in at least one
20 dimension.

3. The coverlay composition in accordance with Claim 1, wherein the sub-micron filler is less than 200 nanometers in at least one
dimension.

25 4. The coverlay composition in accordance with Claim 1, wherein the sub-micron filler is selected from a group consisting of oxides, nitrides, carbides and combinations thereof.

30 5. The coverlay composition in accordance with Claim 1, wherein the sub-micron filler is acicular titanium dioxide, talc, SiC fiber, platy Al₂O₃ or mixtures thereof

6. The coverlay composition in accordance with Claim 1, wherein the polyimide is derived from:

- 5
- a) at least 70 mole percent of the aromatic dianhydride component is pyromellitic dianhydride; and
 - b) at least 70 mole percent of the aromatic diamine component is 4,4'-diaminodiphenyl ether.

7. The coverlay composition in accordance with Claim 6, wherein the sub-micron filler is acicular titanium dioxide, talc, SiC fiber, platy Al₂O₃ or mixtures thereof.

8. The coverlay composition in accordance with Claim 1, wherein:

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- a) at least 75 mole percent of the aromatic dianhydride component is pyromellitic dianhydride; and
- b) 70 mole percent 4,4'-diaminodiphenyl ether and 30 mole percent 1,4 diaminobenzene as the aromatic diamine component.

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9. The coverlay composition in accordance with claim 1 wherein the polyimide is a block copolymer.

10. The coverlay composition in accordance with claim 9 wherein the block copolymer is derived from 4,4'-diaminodiphenyl ether and 1,4 diaminobenzene with pyromellitic dianhydride and 3,3',4,4'-biphenyl tetracarboxylic dianhydride.

11. The coverlay composition in accordance with claim 9 wherein the block copolymer is derived from:

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- a) 10 to 40 mole percent blocks of pyromellitic dianhydride and 1,4 diaminobenzene;

- b) 90 to 60 mole percent blocks of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

12. The coverlay composition in accordance with claim 11,
5 wherein the sub-micron filler is acicular titanium dioxide, talc, SiC fiber, platy Al₂O₃ or mixtures thereof.

13. The coverlay composition in accordance with claim 1,
10 wherein the sub-micron filler is coated with a coupling agent, a dispersant or a combination thereof.

14. The coverlay composition in accordance with claim 1,
wherein the adhesive layer is an epoxy resin selected from the group
consisting of: bisphenol A epoxy resins; bisphenol F epoxy resins;
15 bisphenol S epoxy resins; phenol novolac epoxy resins; cresol novolac epoxy resins; biphenyl epoxy resins; biphenyl aralkyl epoxy resins; aralkyl epoxy resins; dicyclopentadiene epoxy resins; multifunctional epoxy resins; naphthalene epoxy resins; phosphorus containing epoxy resins; rubber modified epoxy resins, and mixtures thereof.

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15. The coverlay composition in accordance with Claim 1
wherein the polyimide is a random copolymer derived from 4,4'-
diaminodiphenyl ether and 1,4 diaminobenzene with pyromellitic
dianhydride and 3,3',4,4'-biphenyl tetracarboxylic dianhydride.

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16. The coverlay composition in accordance with Claim 1
wherein the polyimide is a random copolymer derived from 4,4'-
diaminodiphenyl ether and 1,4 diaminobenzene with pyromellitic
dianhydride.

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/057423

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08G73/10 C09D179/08 H01L21/77 H01L23/14 H01L23/29
 H05K1/03
 ADD.
 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 C09D H01L H05K

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,P	WO 2009/142938 A1 (DU PONT [US]; AUMAN BRIAN C [US]; BOUSSAAD SALAH [US]; CARNEY THOMAS E) 26 November 2009 (2009-11-26) claims page 1, line 11 page 3, line 30 - line 31 -----	1-16
X,P	US 2009/288699 A1 (AUMAN BRIAN C [US] ET AL) 26 November 2009 (2009-11-26) examples -----	1-16
A	US 6 620 339 B1 (SHIMIZU ITSUO [JP] ET AL) 16 September 2003 (2003-09-16) examples -----	1-16
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Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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.</p> <p>"&" document member of the same patent family</p>
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Date of the actual completion of the international search 13 April 2011	Date of mailing of the international search report 19/04/2011
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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 West, Nuki
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/057423

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