Abstract:

Title: MANUFACTURING METHOD FOR POLYIMIDE MOLDED BODY

A method is provided for using polyimide film that has been completely imidized in a manufacturing method for a polyimide molded body, including grinding a polyimide film containing a biphenyl tetracarboxylic acid component as a polyimide acid component to a volumetric average particle diameter of 200 µm or less, and molding essentially only this powder.
MANUFACTURING METHOD FOR POLYIMIDE MOLDED BODY

This application claims priority to Japanese Patent Application 2009-291937 filed December 24, 2009, which is incorporated by reference in its entirety.

The present invention relates to a method for manufacturing a polyimide molded body involving recycling only polyimide film which is difficult to recycle alone.

Polyimide films are engineering plastics with excellent heat resistance, mechanical properties, sliding properties, and chemical resistance, and are used in a variety of fields focusing on electric and electronic device applications. Many thermoplastic engineering plastics such as polypropylene and polyethylene terephthalate can be recycled by heating and melting, and then molding either alone or after blending with unused material.

In contrast, polyimide films generally differ from the aforementioned engineering plastics because they do not have a clear melting point, are non-thermoplastic, and although they are resistant to chemicals such as organic solvents, recycling by heating and melting or the like is not possible. Therefore, the ears and ends of a polyimide film as well as polyimide films that cannot be used as products for other reasons are usually treated as waste.

In order to recycle these polyimide films, a method of chopping the polyimide film to form small pieces and blending in a polyamic acid solution to between approximately 2 and 70 weight percent and then fabricating a polyimide sheet from the polyamic solution containing the small pieces (Japanese Unexamined Patent Application 2006-131753), and a method of a mixture containing between 10 and 99 weight parts of polyimide resin raw powder and
between 1 and 90 weight parts of ground film or resin molded product primarily containing recycled polyimide to obtain a polyimide resin molded part (Japanese Unexamined Patent Application 2006-232996) have been proposed. These small pieces and ground films used polyimide where imidization is complete and forming a molded body using only polyimide powder was not possible. Therefore, these documents have a problem with the cost of recycling and the like because new polyamic acid and polyimide powder that has not been completely imidized are used in addition to the recycled polyimide film, and in order to recycle, new polyamic acid and polyimide powder must be produced.

On the other hand, polyimide films that contain biphenyl tetracarboxylic acid component as the polyimide acidic component are well-known (Japanese Unexamined Patent Application 2005-19159). However, grinding these films and recycling is not described, and even if recycling is performed, other components are added to create an easy molding condition, and using only polyimide film for molding is not mentioned.

**SUMMARY OF THE INVENTION**

In light of the foregoing problems with conventional technology, the present invention provides a method for solely using polyimide film that has been completely imidized.

The present invention uses the following means in order to resolve the aforementioned problems. In other words, the present invention is:

(1) a manufacturing method for a polyimide molded body, which includes grinding a polyimide film containing a biphenyl tetracarboxylic acid component as a polyimide acid component to a volumetric average particle diameter of 200 μm or less, and molding essentially only this powder;

(2) the manufacturing method for a polyimide molded body according to (1), wherein the amount of biphenyl tetracarboxylic acid component is between 2 and 100 mol% with regard to all acidic components; and
(3) The manufacturing method for a polyimide molded body according to (1) or (2), wherein a flexural elongation and tensile elongation of the molded body are both 2% or higher.

**DETAILED DESCRIPTION OF THE INVENTION**

The manufacturing method for a polyimide molded body according to the present invention can provide a desired polyimide molded body by recycling polyimide film which conventionally cannot be recycled alone.

Furthermore, when recycling, a molded body can be formed without using other polyimide resins or powders or the like other than the polyimide film and producing new polyimide resin or powder for recycling is not necessary, so the number of steps for recycling can be greatly decreased.

The present invention will be described below in detail.

The present invention is a manufacturing method for a polyimide molded body, which includes grinding a polyimide film containing a biphenyl tetracarboxylic acid component as a polyimide acid component to a volumetric average particle diameter of 200 μm or less, and molding essentially only this powder. Note, in the present invention, "acid component" is a general term that includes "acid" and "acid dihydrates", while "acid component" in polymers of films or the like refers to "acidic residual groups derived from acid components" that are a component of the polymer. The polyimide film is normally produced by reacting a tetracarboxylic dianhydride compound and a diamine compound in an organic solvent and spreading the polyamic acid solution obtained on a supporting body to promote imidization. In the present invention, the tetracarboxylic acid component contains at least biphenyl tetracarboxylic acid. The amount of biphenyl tetracarboxylic acid used is preferably between 2 and 100 mol% of the total acid component, but lower limits of 5 mol%, 15 mol%, and 25 mol% are successively more preferable. Examples of the biphenyl tetracarboxylic acid component that can be used include 3,3',4,4'-biphenyl tetracarboxylic acid, 2,3',3,4'-biphenyl tetracarboxylic acid, and 2,2',3,3'-biphenyl tetracarboxylic acid as well as amide forming derivatives and acidic anhydrides thereof. Of these, the most preferable biphenyl tetracarboxylic acid component is
3,3',4,4'-biphenyl tetracarboxylic dianhydride. This biphenyl tetracarboxylic acid component can be used individually, or two or more types can be used in combination, and other acid components can be used in combination.

Acid components that can be used in combination include anhydrides of pyromellitic acid, 3,3',4,4'-benzophenone tetracarboxylic acid, oxydiphthalic acid, 2,3,6,7-naphthalene dicarboxylic acid, 2,2-bis(3,4-dicarboxyphenyl) ether, pyridine-2,3,5,6-tetracarboxylic acid and amide forming derivatives thereof.

Examples of the diamine component that forms the polyimide of the present invention include paraphenylene diamine, metaphenylenediamine, benzidine, paraxyylene diamine, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 3,3'-diaminodiphenyl ether, 1,4-bis(4-aminophenoxy) benzene, 1,3-bis(4-aminophenoxy) benzene, 1,3-bis(3-aminophenoxy) benzene, 2,2-bis(4-aminophenoxy) phenyl propane, bis[4-(4-aminophenoxy) phenyl] sulfone, bis[4-(3-aminophenoxy) phenyl] sulfone, 4,4'-bis (4-aminophenoxy) biphenyl, and 4,4'-bis(3-aminophenoxy) biphenyl as well as amide forming derivatives thereof. Of these, paraphenylene diamine and 4,4'-diaminodiphenyl ether are preferable. These diamine components can be used individually, or two or more types can be used in combination.

A manufacturing method for typical polyimide films is described below. A diamine such as 4, 4'-diamino diphenyl ether, 3, 4'-diamino diphenyl ether, or para-phenylene diamine is placed in a separable flask, either individually or in combination, and then an organic solvent such as N,N-dimethylacetamide is added and mixed at room temperature under a nitrogen gas environment. After mixing for approximately 1 hour, 3,3',4,4'-biphenyl tetracarboxylic dianhydride and pyromellitic dianhydride are added in multiple parts and after additional mixing for approximately 1 hour, a N,N-dimethylacetamide solution of pyromellitic dianhydride is added by drops over 30 minutes, and mixing is performed for approximately 1 hour to obtain a polyamic acid solution. The polyamic acid obtained is placed on a polyester film and a uniform film is formed using a spin coater. This sample is heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film. The self-supporting polyamic acid film is
peeled from the polyester film and secured in a metal frame, and then heat-treated at a temperature between 200 and 400°C in order to obtain a polyimide film.

Note, the polyimide film can be an industrially mass-produced polyimide film so long as the polyimide film contains a biphenyl tetracarboxylic acid component as an acid component.

In the present invention, the polyimide film is ground. The grinder can be a freezer mill, a ball mill, a bead mill, a sand mill, a jet mill, a turbo mill, an atomizer mill, or an impact mill, etc., and a plurality of different grinders can be used in combination. Furthermore, prior to crushing the polyimide film can be heated or chemically treated in order to aid in grinding, and the polyimide film can be cut or the like to achieve a desired size. It is important that the ground particles be a fine powder and the size must be such that the volumetric average particle diameter is 200 μm or less, more preferably between 10 and 150 μm, and even more preferably between 15 and 80 μm. This is because if the volumetric average particle diameter is larger than 200 μm, the bulk density will be high, and when a molded body is formed, sufficient density will not be achieved. The density of the resin is related to the strength of the molded body, and the resin will be brittle if sufficient density is not achieved.

As described above, the main characteristic of the present invention is that the polyimide powder obtained can essentially be molded alone. Conventional polyimide films cannot be molded alone, even when powdered. The term "essentially" means that the polyimide film can be used alone, or a small amount of other substances such as polyimide films other than those polyimide films designated by the present invention can be included.

The method of molding the polyimide powder of the present invention is not particularly restricted, and for example a heated press that simultaneously heats and compresses can be used. Furthermore, the powder that is used can be dried prior to molding, or premolding can be performed using only pressure without heat prior to heat pressing. Furthermore, these processes can be performed under an environment that uses an inert gas such as nitrogen gas.
The molded body obtained preferably has equivalent physical properties as a normal polyimide molded body, and the flexural elongation and tensile elongation are preferably 2% or higher. The flexural elasticity is preferably 2 GPa or higher, and the flexural strength is preferably 50 MPa or higher.

Examples
The present invention will be described in detail using the following examples. However, the present invention is not restricted to these examples. Note, the physical properties of these examples were measured by the following methods.

<Volumetric Average Particle Diameter>
The measurement was taken using an LMS-30 laser type particle distribution analyzer manufactured by Seishin Entprise Co., Ltd.

<Flexural Elongation>
The measurement was performed in accordance with ASTM D790.

<Tensile Elongation, Tensile Strengths>
The measurement was performed in accordance with ASTM D1708.

Example 1
(Manufacturing the polyimide film)
12.94 g (0.065 mol) of 4, 4'-diamino diphenyl ether, 6.99 g (0.065 mol) of paraphenylene diamine, and 189.32 g of N,N-dimethylacetamide were added to a 300 ml separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 13.32 g (0.045 mol) of 3,3',4,4'-biphenyl tetracarboxylic dianhydride and 14.11 g (0.065 mol) of pyromellitic dianhydride were added in multiple parts, and after mixing for another 180 minutes, 14.09 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent) was added by drops over 30 minutes, and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.
A portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film. The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film. The film thickness at this time was 53 µm.

(Manufacturing the polyimide powder)

The polyimide film obtained by the aforementioned method was shredded using a shredder, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Entriprise Co., Ltd., the average volumetric diameter was 63 µm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm² (approximately 2 x 10E5 newtons/cm²), and this condition was maintained for 30 minutes to obtain a molded body. The physical properties of the molded body obtained are shown in Table 1.

Example 2

(Manufacturing the polyimide film)

20.02 g (0.100 mol) of 4,4'-diamino diphenyl ether and 182.98 g of N,N-dimethylacetamide were added to a 300 ml separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 28.54 g (0.097 mol) of 3,3',4,4'-biphenyl tetracarboxylic dianhydride was added in multiple parts, and after mixing for another 120 minutes, 10.9 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent) was added by drops over 30 minutes,
and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.

A portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film.

The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film. The film thickness at this time was 42 µm.

(Manufacturing the polyimide powder)

This polyimide film was shredded using a shredder, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Enterprise Co., Ltd., the average volumetric diameter was 70 µm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm², and this condition was maintained for 30 minutes to obtain a molded body. The physical properties of the molded body obtained are shown in Table 1.

Example 3

(Manufacturing the polyimide film)

14.06 g (0.130 mol) of paraphenylenediamine and 190.87 g of N,N-dimethylacetamide were added to a 300 ml separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 37.10 g (0.126 mol) of 3,3',4,4'-biphenyl tetracarboxylic dianhydride was added in multiple parts, and after mixing for another 120 minutes, 14.18 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent) was added by drops over 30 minutes,
and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.

The portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film.

The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film.

The film thickness at this time was 48 μm.

(Manufacturing the polyimide powder)

This polyimide film was shredded using a shredder, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Entriprise Co., Ltd., the average volumetric diameter was 68 μm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm², and this condition was maintained for 30 minutes to obtain a molded body. The physical properties of the molded body obtained are shown in Table 1.

Example 4

(Manufacturing the polyimide film)

23.03 g (0.115 mol) of 4,4'-diamino diphenyl ether and 185.69 g of N,N-dimethylacetamide were added to a 300 ml separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 8.46 g (0.028 mol) of 3,3',4,4'-biphenyl tetracarboxylic dianhydride and 18.06 g (0.082 mol) of pyromellitic dianhydride were added in multiple parts, and after mixing for another 120 minutes, 12.54 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent)
was added by drops over 30 minutes, and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.

The portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film.

The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film. The film thickness at this time was 47 µm.

(Manufacturing the polyimide powder)

This polyimide film was shredded using a shredder, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Enterprise Co., Ltd., the average volumetric diameter was 65 µm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm², and this condition was maintained for 30 minutes to obtain a molded body. The physical properties of the molded body obtained are shown in Table 1.

Comparative Example 1

(Manufacturing the polyimide film)

25.03 g (0.1 25 mol) of 4, 4′-diamino diphenyl ether and 192.50 g of N,N-dimethylacetamide were added to a 300 mL separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 26.45 g (0.121 mol) of pyromellitic dianhydride was added in multiple parts, and after mixing for another 120 minutes, 13.63 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent) was added by drops over 30 minutes, and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.
The portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film.

The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film. The film thickness at this time was 55 μm.

(Manufacturing the polyimide powder)

The polyimide film was shredded using a shredder, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Enterprise Co., Ltd., the average volumetric diameter was 63 μm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm², and this condition was maintained for 30 minutes, but the particle cohesion was insufficient so a molded body was not obtained.

Comparative Example 2

(Manufacturing the polyimide film)

20.02 g (0.100 mol) of 4, 4’-diamino diphenyl ether and 182.98 g of N,N-dimethylacetamide were added to a 300 ml separable flask equipped with a chemical stirrer, and mixed at room temperature under a nitrogen gas environment. After mixing for 60 minutes, 28.54 g (0.097 mol) of 3,3’,4,4’-biphenyl tetracarboxylic dianhydride was added in multiple parts, and after mixing for another 120 minutes, 10.9 g of a N,N-dimethylacetamide solution of pyromellitic dianhydride (6 weight percent) was added by drops over 30 minutes, and mixing was performed for an additional 60 minutes to obtain a polyamic acid solution.
The portion of the polyamic acid obtained was placed on a polyester film and a uniform film was formed using a spin coater. This sample was heated and dried in an oven for 1 hour at 100°C to obtain a self-supporting polyamic acid film. The self-supporting polyamic acid film was peeled from the polyester film and secured in a metal frame, and then heat-treated at 200°C for 30 minutes, 300°C for 20 minutes, and then 400°C for 5 minutes to obtain a polyimide film. The film thickness at this time was 42 µm.

(Manufacturing the polyimide powder)

This polyimide film was shredded using shears, and then ground in a jet mill. When the powder obtained was measured using a LMS-30 laser particle distribution analyzer manufactured by Seishin Entriprise Co., Ltd., the average volumetric diameter was 252 µm.

(Manufacturing the molded body)

A molded body was manufactured from this powder using a heated press method. The powder was placed in a molder and the temperature was increased to 400°C while applying a force of 2.0 ton/cm², and this condition was maintained for 30 minutes, but the particle cohesion was insufficient so a molded body was not obtained.
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4,4'-ODA: 4,4'-diaminodiphenyl ether  
PPD: Paraphenyleneamine  
PMDA: Pyromellitic dianhydride  
PDA: 3,3',4,4'biphenyltetracarboxylic dianhydride
Table 1- continued

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4,4'-ODA: 4,4'-diaminodiphenyl ether

PPD: Paraphenyleneamine

PMDA: Pyromellitic dianhydride

PDA: 3,3',4,4'biphenyltetraconoxylic dianhydride
The polyimide powder of the present invention can manufacture a molded body that is equivalent to existing polyimide molded bodies, using only the manufactured powder, and therefore a resin equivalent to an existing polyimide molded body can be manufactured using only polyimide film for recycling.
What is claimed is:

1. A manufacturing method for a polyimide molded body, comprising grinding a polyimide film containing a biphenyl tetracarboxylic acid component as a polyimide acid component to a volumetric average particle diameter of 200 μm or less, and molding essentially only this powder.

2. The manufacturing method for a polyimide molded body according to claim 1, wherein the amount of biphenyl tetracarboxylic acid component is between 2 and 100 mol% with regard to all acidic components.

3. The manufacturing method for a polyimide molded body according to claim 1 or 2, wherein a flexural elongation and a tensile elongation of the molded body are both 2% or higher.
### INTERNATIONAL SEARCH REPORT

**International application No:**

PCT/US2010/061696

**A. CLASSIFICATION OF SUBJECT MATTER**

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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)

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<td>JP 2006 232996 A (TOYAY INDUSTRIES) 7 September 2006 (2006-09-07) cited in the application * abstract paragraphs [0015], [0019], [0021], [0046]; claims -----</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

**Date of the actual completion of the international search:**

30 March 2011

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Otegui Rebol I o, Juan
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