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(21) International Application Number: PCT/US97/14512 (22) International Filing Date: 19 August 1997 (19.08.97) (30) Priority Data: 08/697,048 19 August 1996 (19.08.96) US (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor: BLOOM, Joy, Sawyer; 29 Country Gates Drive, Wilmington, DE 19810 (US). (74) Agent: MOYLES, Lisa, J.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, CA, CN, JP, KR, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: POLYIMIDE POLYMERIC BLENDS (57) Abstract New polyimide polymeric blends which are environmentally friendly during compounding and give improved coefficient of friction in shaped articles prepared therefrom are provided by blending polyimides which are at least 90 % imidized and substantially solvent free and have a mean particle size of bout 30 μ m or less with at least one melt processible thermoplastic liquid crystalline polymer or polyamide and a lubricant.		

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TITLE**POLYIMIDE POLYMERIC BLENDS****BACKGROUND OF THE INVENTION**

5 The present invention relates to blends of polyimides having a controlled particle size with thermoplastic polymers and a lubricant.

There are several examples in the literature of thermoplastic and polyimide blends having improved properties. For the most part the polyimide in these blends is thermoplastic. Such is the case in US Pat. No. 5,135,990 and EP 0 430 640 A1.

10 Where the polyimide of the prior art is in the form of polyamic acid it will generally contain solvent. Commonly the solvent content can be from 10-30 weight percent. The presence of more than very small amounts of solvent results in the release of volatiles during the completion of the imidization reaction and creates environmental problems during processing.

15 It is desirable for environmental purposes to eliminate polyamic acid containing solvents from polyimide polymers and utilize a fully imidized polyimide or one having a high degree of imidization. By using the present invention, superior properties can be attained using polyimides which are at least about 90% imidized or are fully imidized.

20 **SUMMARY OF THE INVENTION**

New polyimide polymeric blends which are environmentally friendly during compounding and give shaped articles which exhibit an improved coefficient of friction are provided by blending particulate polyimides which are substantially solvent free, have a controlled particle size and which are at least
25 about 90% imidized with at least one melt processible thermoplastic polymer and a lubricant. By substantially solvent free it is meant that the solvent content is not greater than about 1 weight percent. More particularly, from about 5 to 40% by weight of a particles of a solvent free polyimide having a mean particle size of about 30 μ m or less prepared from at least one aromatic diamine and at least one
30 aromatic dianhydride in which at least about 90% of the polymeric units are converted to polyimide are blended with from about 40 to 93 weight % of at least one non-fluorine containing thermoplastic polymer which is melt processible at a temperature of less than about 400°C. and from about 2 to 40% by weight of a lubricant such as tetrafluoroethylene polymers and copolymers (hereinafter
35 referred to as PTFE), graphite or molybdenum disulfide or combinations thereof.

Preferably, at least 25% of the polyimide particles should have a size less than 20 μ m, and the compositions contain from about 8-24 weight % polyimide and from about 56-72 weight % thermoplastic polymer. In order to achieve the benefits of this invention the particle size of the polyimide must be preserved during processing and retained in the shaped articles.

DETAILED DESCRIPTION

A wide variety of polyimide resins which have a particle size about 30 μ m or less and which are at least 90% imidized can be used in the present invention. Aromatic polyimides, such as those described in U.S. Pat. Nos. 3,179,614 and 4,622,384 can be used. Certain of those polyimides have been found to be particularly satisfactory in the present invention, namely, those having a rigid polymeric structure. Representative of such rigid polymeric materials are those prepared using aromatic diamines and anhydrides such as m-phenylene diamine (MPD); bis-4,4'(3 aminophenoxy)biphenyl; 3,4-oxydianiline (3,4-ODA); oxydianiline (ODA); p-phenylene diamine (PPD); benzophenone-3,3',4,4'-tetracarboxylic dianhydride (BTDA); bis phenol-A-diphthalicanhydride (BPADA); pyromellitic dianhydride (PMDA); and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA). The dianhydride and the aromatic diamine may be reacted in substantially equimolar quantities. However, excesses of dianhydride or diamine can be used to beneficially modify the properties of the final polyimide. The reaction product of the dianhydride and the aromatic diamine is a polyimide precursor resin, containing a limited amount of polyamic acid which can be thermally or chemically converted to polyimide according to known techniques. Polyimide particles having a mean particle size of about 30 μ m or less can be prepared from polyimides having larger sizes by grinding and classifying the larger sized polyimides.

At least one non-fluorine containing polymer which is melt processible at temperatures of less than about 400°C. can be blended with the polyimide resin. Melt processible is used in its conventional sense, that the polymer can be processed in extrusion apparatus at the indicated temperatures without substantial degradation of the polymer. A lubricant is included in the blending operation.

Polyamides which can be used include nylon 6, nylon 6,6, nylon 610, nylon 612 and aromatic polyamides. Polyesters include polybutylene terephthalate and polyethylene terephthalate.

The melt processible polyesters are preferably in the form of liquid crystalline polymers (LCPs). The LCPs are generally polyesters including, but not limited to polyesteramides and polyesterimides. LCPs are described in Jackson et al. in U.S. Pat. Nos. 4,169,933, 4,242,496, and 4,238,600, as well as in
5 "Liquid Crystal Polymers: VI Liquid Crystalline Polyesters of Substituted Hydroquinones", Contemporary Topics in Polymer Science, 1984, Vol. 5, pp. 177-208. Others are described in Calundann, U.S. Pat. No. 4,219,461. Particularly desirable LCPs are prepared from monomers such as phenyl hydroquinone, hydroquinone, t-butyl hydroquinone, 1,4-benzene dicarboxylic
10 acid, 1,3-benzene dicarboxylic acid, 4-hydroxybenzoic acid and 2,6-naphthalene dicarboxylic acid in varying ratios.

One or more of known lubricants for polyimide compositions may be used in the compositions of this invention such as, graphite, molybdenum disulfide or PTFE. Nonfibrillating tetrafluoroethylene polymers and copolymers
15 such as tetrafluoroethylene/hexafluoropropylene are also useful and are commercially available in micropowder form. E.I. du Pont de Nemours and Company sells such materials under its trademark, Teflon® MP. Preparation of copolymers of tetrafluoroethylene is described in Morgan U.S. Pat. No. 4,879,362.

The present polymeric compositions may include additives in addition
20 to a lubricant, such as calcium carbonate, glass beads, zinc oxide, and fiber reinforcements such as ceramic fibers, aramid fibers, potassium titanate fibers, glass fibers and carbon fibers. The particular additive selected will depend on the effect desired.

High performance shaped articles are formed from the polymeric
25 blends of this invention by a suitable molding operation such as injection or compression molding. Molding conditions must be selected to prevent coalescing or degrading the polyimide particles thereby preserving their integrity in the shaped article.

The present invention is further illustrated by the following Examples
30 in which parts and percentages are by weight unless otherwise indicated. In the Examples wear specimens were prepared by machining test blocks of the composition described. A 6.35mm (0.25") wide contact surface of a wear/friction test block was machined to such a curvature that it conformed to the outer circumference of a 35mm (1.38") diameter X 8.74mm (0.34") wide metal mating
35 ring. The blocks were oven dried and maintained over desiccant until tested.

Wear tests were performed using a Falex No. 1 Ring and Block Wear and Friction Tester. The equipment is described in ASTM Test method D2714. After weighing, the dry block was mounted against the rotating metal ring and loaded against it with the selected test pressure. Rotational velocity of the ring was set at the desired speed. No lubricant was used between the mating surfaces. The rings were SAE 4620 steel, Rc 58-63, 6-12 RMS. A new ring was used for each test. Test time was 24 hours, except when friction and wear were high, in which case the test was terminated early. The friction force was recorded continuously. At the end of the test time, the block was dismounted, weighed, and the wear calculated by the following calculation:

Wear Volume Calculation

$$\text{wear volume(cc/hr)} = \frac{\text{weight loss (grams)}}{\text{material density(g/cc)} \times \text{test duration(hr)}}$$

A low number is desired for Wear Volume and a low number or narrow range is desired for the Coefficient of Friction. Coefficient of Friction appears to be directly correlated to the particle size of the polyimide in the polymer matrix.

Particle size was determined through the use of a Coulter LS 130 Laser Diffraction Analyzer. A garnet standard of 109 μm and a Fraunhofer (Optical Model) was used.

Tensile properties were measured according to ASTM D638, and flexural properties were measured according to ASTM D-790.

EXAMPLES

SUMMARY OF POLYIMIDES USED IN EXAMPLES (averages of several samples)

Type	Method Used to Prepare	Monomers	Mean Particle Size (μm)
A	US 4,622,614	ODA/PMDA	75.4
B	US 4,622,614	ODA/PMDA	75.4
C	US 3,179,384	ODA/PMDA	29.6
D	US 3,179,384	ODA/PMDA	29.6
E		ODA/BTDA	23.8

The solvent content of polyimide types B, C, D and E was <1 weight %.

EXAMPLE 1 (Comparative)

56 parts of a liquid crystalline polyester (DuPont Zenite® 6000) was blended with 20 parts PTFE (DuPont Teflon® MP-1600 micropowder and with 24 parts of polyimide resin prepared from pyromellitic dianhydride and 4,4' -oxydianiline present as its precursor, polyamic acid, (this polyimide type is referred to as "A") having a mean particle size of 75 μm , or with 24 parts of fully imidized polyimide resin prepared in the same manner having a mean particle size of 75 μm (this polyimide type is referred to as "B"). The blending was accomplished using a 30mm twin screw extruder with barrels set to 290°C and the die at 335°C having vent ports in zones 4, 6 and 8. Quenching was accomplished using a water spray. The strand was cut into pellets using a standard rotating blade cutter. The pellets were molded into standard 6.4 mm thick ASTM (D638) tensile test bars using a 170 g capacity, 145 ton clamping pressure injection molding machine. The profile was as follows: Rear 313°C, Center 334°C, Front 335°C and Nozzle 332°C, Boost 1 sec, Injection 20 sec, Hold 20 sec, Injection Pressure 3.4 MPa, Ram Speed fast, Screw Speed 107 rpm and Back Pressure minimum.

The samples were made into the test specimens by machining. Wear testing was done at a PV of 1.75 MPa-m/s (1.28MPa, 1.36 m/s)

Sample No	Polyimide Type	Wear Volume cc x 10 ⁻⁴ /hr	Coefficient of Friction	Tensile Strength (MPa)	Elong. (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
I	A*	25.7	0.21-0.33	42.6	2.5	71.4	4013
II	B	24.9	0.23-0.33	40.7	2.3	71.9	4079

*Solvent content 25.05 weight %

EXAMPLE 2

The same method for sample preparation as used in Example 1 was utilized except that one of the polyimides used were prepared from polyimide pyromellitic dianhydride and 4,4' -oxydianiline having an imidization level of about 90% and a mean particle size of 30 μm (polyimide type "C") , and type "D" had a imidization level >99.9% and a mean particle size of 30 μm .

Sample No	Polyimide Type	Wear Volume cc x 10 ⁻⁴ /hr	Coefficient of Friction	Tensile Strength (MPa)0.7 hr	Elong. (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
III	C	5.0	0.25-0.32	68.5	3.2	91.4	5054
IV	D	3.7	0.24-0.27	47.0	2.6	70.3	4308
V	A*	5.9	0.28-0.33	46.7	2.4	70.7	4188

*Solvent content 24.19 weight %

10 EXAMPLE 3

The same method for sample preparation as used in Example 2 was utilized except that DuPont's Zenite® 7000 liquid crystalline polymer was utilized in place of Zenite® 6000 and 10 parts zinc oxide additive (obtained from Matsushita as WZ-511 powder) having a starting mean particle size of 2.1 µm and 10 parts PTFE (DuPont Teflon® MP-1600 micropowder) were utilized. The polyimides used were types "A", "C" and "E". "E" was prepared from benzophenone -3,3',4,4' - tetracarboxylic dianhydride and 4,4' -oxydianiline present as >90% imidized having a mean particle size of 24 µm. The amount of LCP and Polyimide used are documented in the table below:

Sample No	Parts LCP	Polyimide Type	Parts polyimide	Wear Volume cc x 10 ⁻⁴ /hr	Coefficient of Friction
VI	72	C	8	2.8	0.22-0.26
VII	64	C	16	4.6	0.22-0.27
VIII	56	C	24	5.9	0.22-0.24
IX	72	D	8	4.7	0.18-0.25
X	64	D	16	5.5	0.22-0.28
XI	56	D	24	5.9	0.21-0.26
Comparison	56	A	24	5.0	0.20-0.29

EXAMPLE 4

56 parts of thermoplastic Polyamide (DuPont Zytel® HTN) were blended with 10 parts zinc oxide additive (obtained from Matsushita as WZ-511 powder) having a starting mean particle size of 2.1 µm, 10 parts PTFE (DuPont Teflon® MP-1600 micropowder) and 24 parts polyimide resin. This was

accomplished using a 30mm twin screw extruder with barrels set to 320°C and the die at 335°C. Quenching was accomplished using a water spray. The strand was cut into pellets using a standard rotating blade cutter. The pellets were molded into standard 6.4 mm thick ASTM (D638) tensile test bars using a 170 g capacity, 145 ton clamping pressure interjection molding machine. The profile was as follows: Rear 315°C, Center 335°C, Front 335°C and Nozzle 335°C; Boost 0.5 sec, Injection 20 sec, Hold 20 sec, Injection Pressure 4.8 MPa, Ram Speed fast, Screw Speed 120 rpm an 0.34 MPa Back Pressure.

Sample No	Polyimide	Wear	Coefficient of Friction	Tensile Strength (MPa)	Elong. (%)	Flexural Strength (MPa)	Flexural Modulus (MPa)
	Type	Volume cc x 10 ⁻⁴ /hr					
XI	E	3.3	0.09-0.22	51.0	2.2	109.8	2983
XIII	A*	2.9	0.11-0.33	37.2	1.7	90.7	2717

*Solvent content 21.56 weight %

WHAT IS CLAIMED IS:

1. A polymeric blend comprised of
 - (a) from about 5 to 40% by weight of particulate polyimide which
5 maintains its particulate form at temperatures of less than 400°C having a mean
particle size of about 30µm or less which is at least about 90% imidized,
 - (b) from about 40 to 93% by weight of at least one non-fluorine containing
thermoplastic polymer which is melt processible at temperatures of less than about
400°C., and
 - 10 (c) from about 2 to 40 % by weight of a lubricant, such that the amount of
components (a), (b) and (c) together make up 100% by weight.
2. The composition of claim 1 wherein said thermoplastic polymer is a
liquid crystalline polymer.
15
3. The composition of claim 1 wherein said thermoplastic polymer is a
polyamide.
- 4 The composition of claim 1 where from about 8 to 24% by weight of
20 said polyimide particles and from about 56 to 72 % by weight of said
thermoplastic polymer are present in said composition.
5. The composition of claim 1 wherein said lubricant is a
tetrafluoroethylene polymer or copolymer of tetrafluoroethylene.
25
6. A shaped article having enhanced coefficient of friction prepared from
the composition of claim 1 wherein the mean particle size of the polyimide in the
shaped article is about 30µm or less.

30

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/14512

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08L67/00 C08L77/00 C08L79/08

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)

IPC 6 C08L

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 94 14895 A (DU PONT) 7 July 1994 see page 1, line 30 - page 6, line 10; claims 1-5,10,16 see page 4, line 4-18 ---	1-6
A	US 4 444 958 A (GILLES RICHARD C) 24 April 1984 see the whole document ---	1,3
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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