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NASA CASE NO. LAR-14194-1

PRINT FIG. #3

NOTICE

25P

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Serial No: 07,344,877

Filed: April 28, 1989

LeRC

(NASA-Case-LAR-14194-1) NOVEL POLYIMIDE COMPOSITIONS BASED ON 4,4': ISOPHTHALOYLDIPHTHALIC ANHYDRIDE (IDPA) Patent Application (NASA) 25 p CSCL 11D
N90-15148
Unclas
G3/24 0256860

NOVEL POLYIMIDE COMPOSITIONS BASED ON 4,4' - ISOPHTHALOYLDIPHTHALIC ANAYDRIDE (IDPA)

AWARDS ABSTRACT

LAR 14194-1

Polyimides have become preeminent as technologically and commercially viable materials for thermally stable heteroaromatic applications due to their versatility, processability and high level of thermooxidative stability. A large number of new compositions are appearing in the patent literature each year. Examples include high performance polyimide adhesives, which are used in the aerospace industry, for example, in joining metals to metals or metals to composite structures. In addition they are rapidly finding new uses as matrix resins for composites, molding powders, and films. These materials display a number of performance characteristics such as high temperature and solvent resistance, improved flow for better wetting and bonding, solvent resistance, high modulus, chemical and hot water resistance, etc. One area of application is in the manufacture of lighter and stronger aircraft and spacecraft structures. Accordingly, the primary object of this invention is the preparation of highly thermooxidatively stable, solvent resistant polyimide compositions.

The present invention relates to a series of twelve high temperature, high performance, linear thermoplastic polyimide compositions based on 4,4' - isophthaloyldiphthalic anhydride (IDPA).

These movel IDPA polyimides typically give high molecular weight materials; films cast from N,N-dimethylacetamide (DMAc) are usually creasable, lightly colored and have glass transition temperatures in the 188-303°C range as determined by differential scanning calorimetry (DSC). They are all insoluble in hot, highly polar solvents like m-cresol and DMAc after a 300°C cure in air. Their long term thermooxidative stability is excellent at 300°C and 350°C in air. Several compositions have been found to be semicrystalline by DSC and wide angle X-ray scattering (WAXS). The polyimide from IDPA and 1,3-bis(4-aminophenoxy-4'-benzoyl)benyene exhibits multiple crystallization and melting behavior, implying the existence of two kinetic and two thermodynamic crystallization and melting transitions by DSC.

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Initial Evaluator: Brian J. Jensen
Serial No: 07/344,877
Filing Date: April 28, 1989

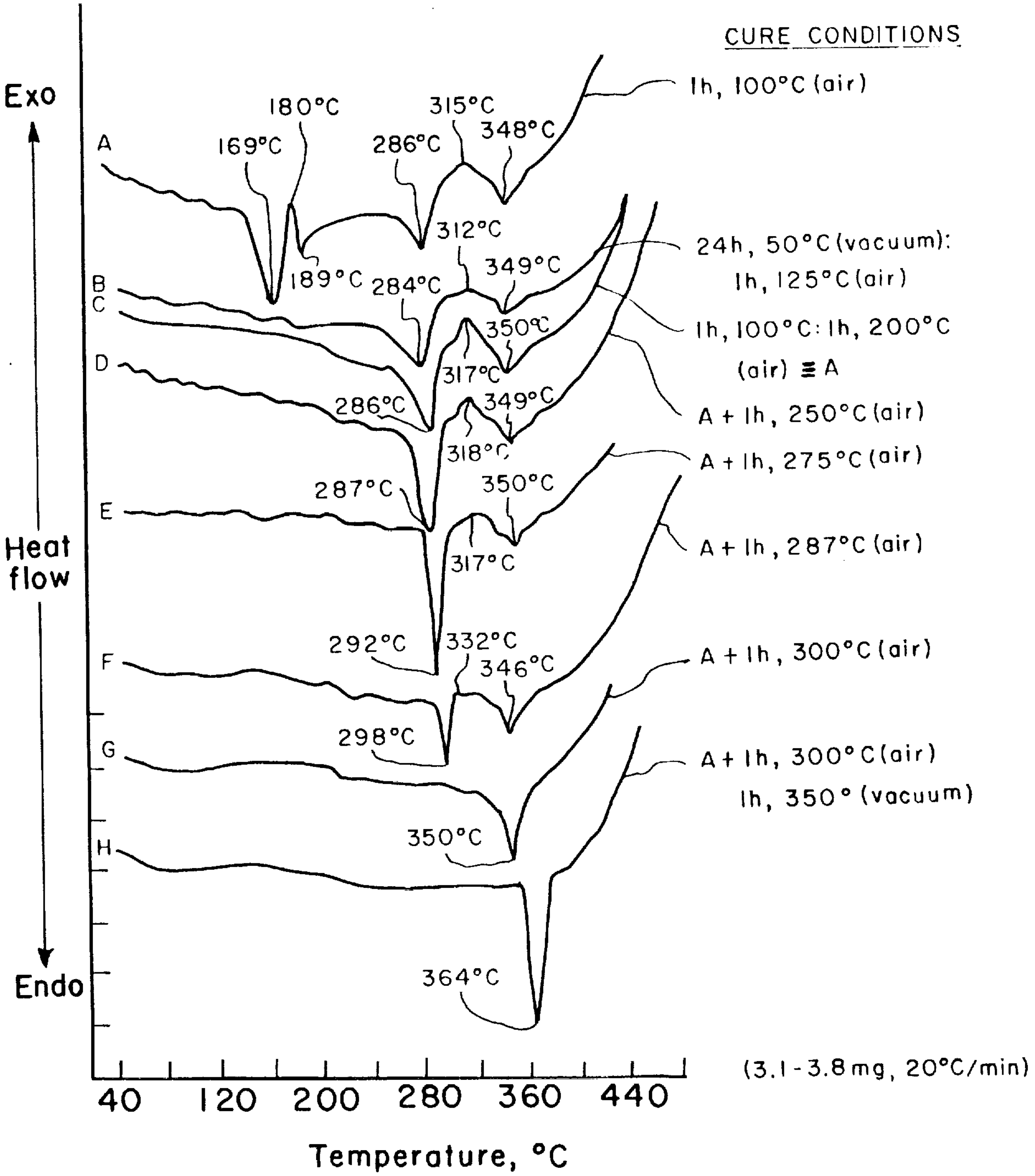

CURE CONDITIONS
Exo
Heat flow
Endo
A
B
C
D
E
F
G
H
169°C
180°C
189°C
286°C
315°C
348°C
312°C
284°C
349°C
350°C
317°C
286°C
349°C
318°C
287°C
350°C
317°C
292°C
332°C
346°C
298°C
350°C
364°C
1h, 100°C (air)
24h, 50°C (vacuum):
1h, 125°C (air)
1h, 100°C: 1h, 200°C
(air) ≡ A
A + 1h, 250°C (air)
A + 1h, 275°C (air)
A + 1h, 287°C (air)
A + 1h, 300°C (air)
A + 1h, 300°C (air)
1h, 350° (vacuum)
(3.1-3.8 mg, 20°C/min)
40
120
200
280
360
440
Temperature, °C

FIG. 1

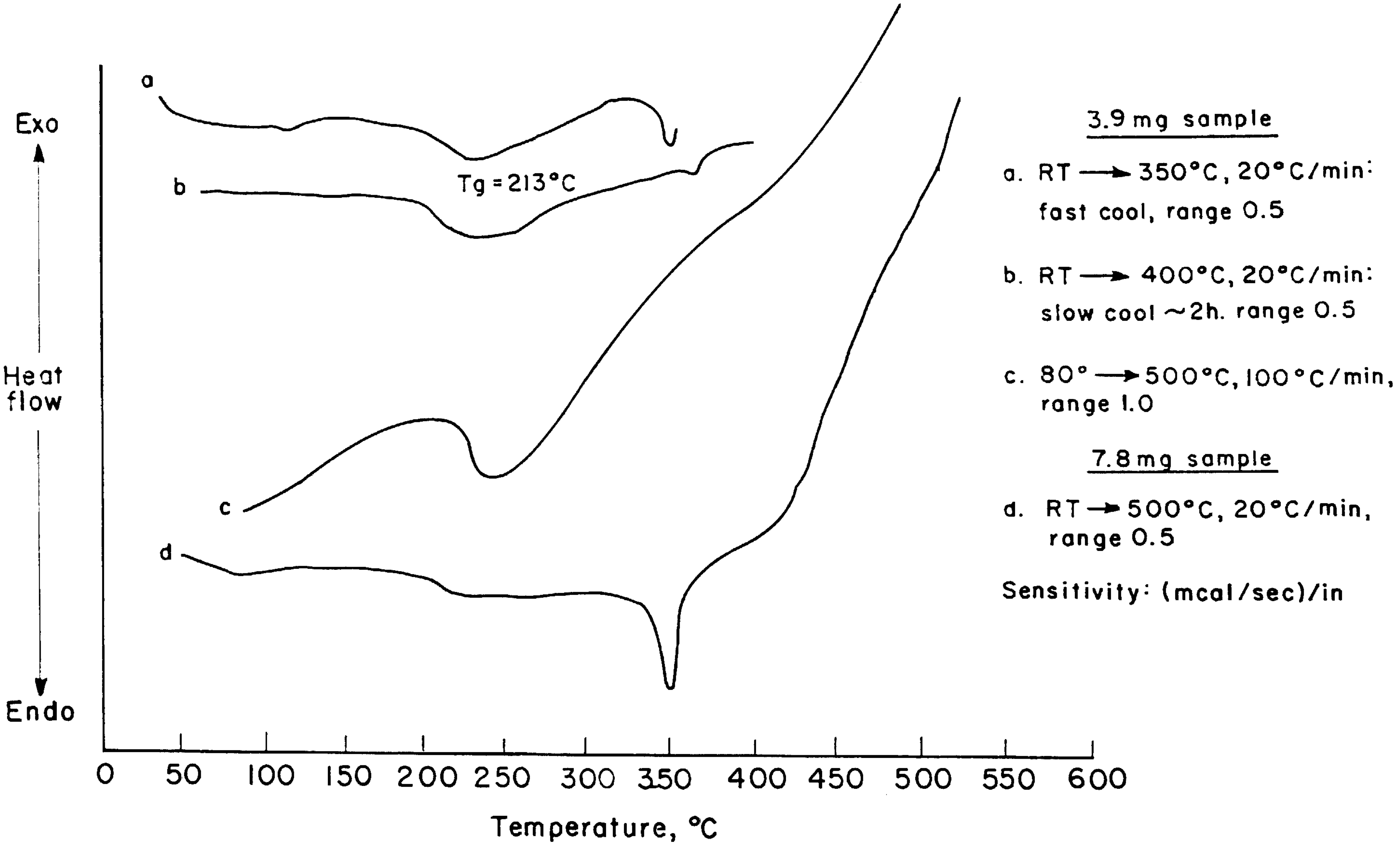

a
b
c
d
Tg = 213°C
Exo
Heat flow
Endo
0
50
100
150
200
250
300
350
400
450
500
550
600
Temperature, °C
3.9 mg sample
a. RT → 350°C, 20°C/min: fast cool, range 0.5
b. RT → 400°C, 20°C/min: slow cool ~2h. range 0.5
c. 80° → 500°C, 100°C/min, range 1.0
7.8 mg sample
d. RT → 500°C, 20°C/min, range 0.5
Sensitivity: (mcal/sec)/in

FIG. 2

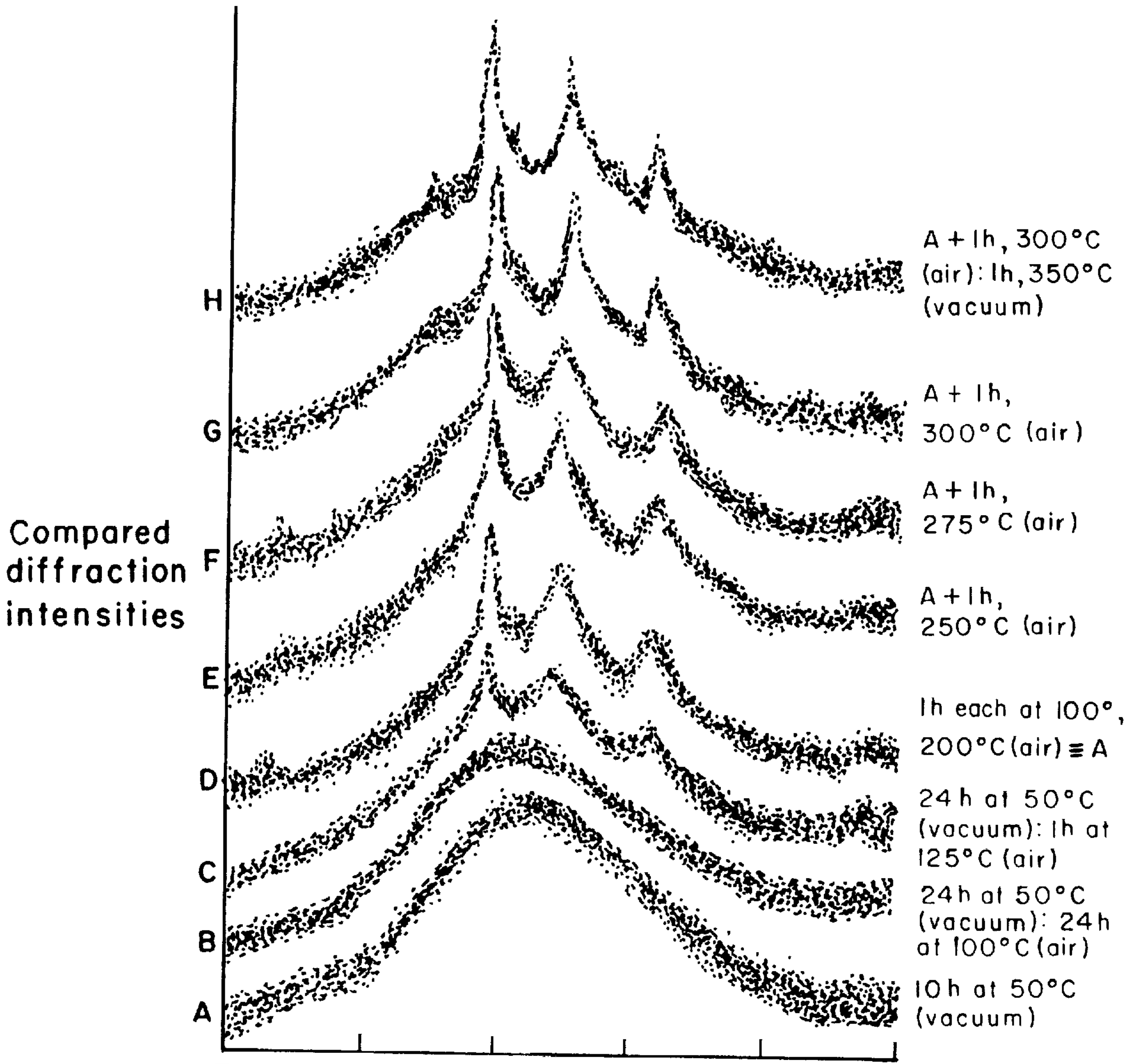

Compared diffraction intensities
H
G
F
E
D
C
B
A
A + 1h, 300°C (air): 1h, 350°C (vacuum)
A + 1h, 300°C (air)
A + 1h, 275°C (air)
A + 1h, 250°C (air)
1h each at 100°, 200°C(air) ≡ A
24 h at 50°C (vacuum): 1h at 125°C (air)
24h at 50°C (vacuum): 24h at 100°C (air)
10h at 50°C (vacuum)
5
12
19
26
33
40
Diffraction angle (2θ)

FIG. 3

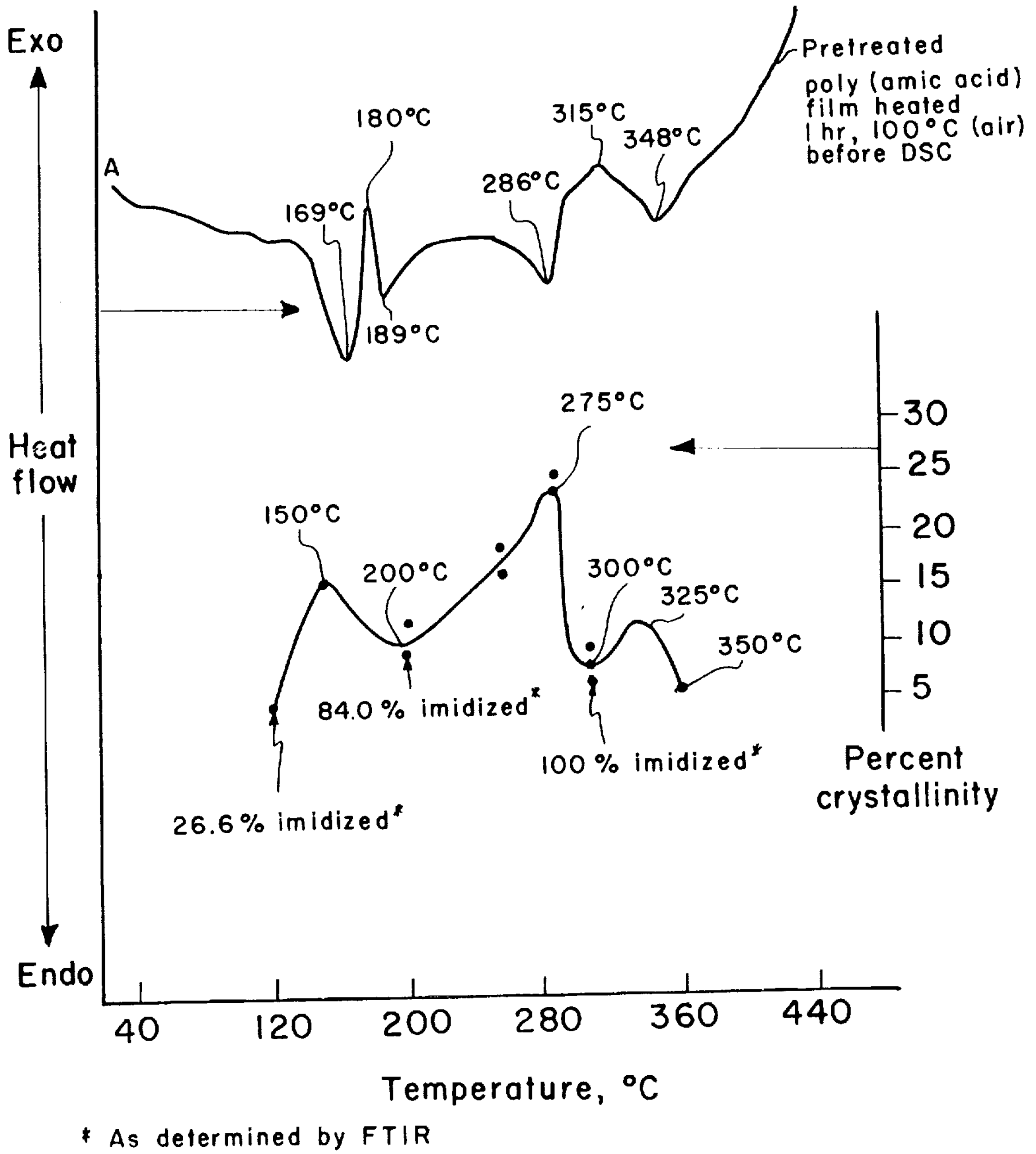

Exo
Heat flow
Endo
A
169°C
180°C
189°C
286°C
315°C
348°C
Pretreated poly (amic acid) film heated 1 hr, 100°C (air) before DSC
150°C
200°C
275°C
300°C
325°C
350°C
84.0 % imidized*
100 % imidized*
26.6 % imidized*
30
25
20
15
10
5
Percent crystallinity
40
120
200
280
360
440
Temperature, °C
* As determined by FTIR

FIG. 4

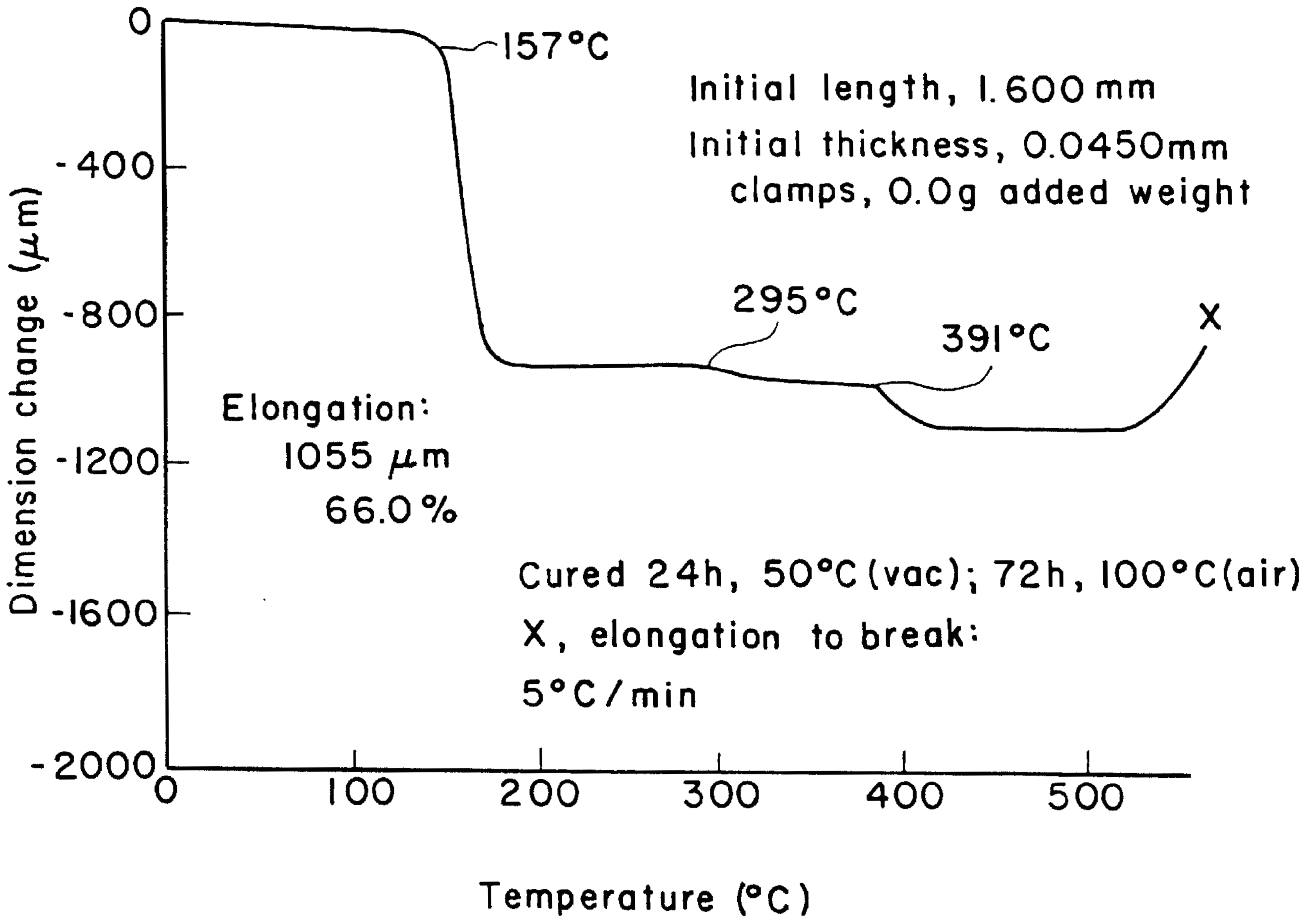

0
-400
-800
-1200
-1600
-2000
Dimension change (μm)
0
100
200
300
400
500
Temperature (°C)
157°C
295°C
391°C
X
Initial length, 1.600 mm
Initial thickness, 0.0450mm
clamps, 0.0g added weight
Elongation:
1055 μm
66.0 %
Cured 24h, 50°C (vac); 72h, 100°C (air)
X, elongation to break:
5°C/min

FIG. 5

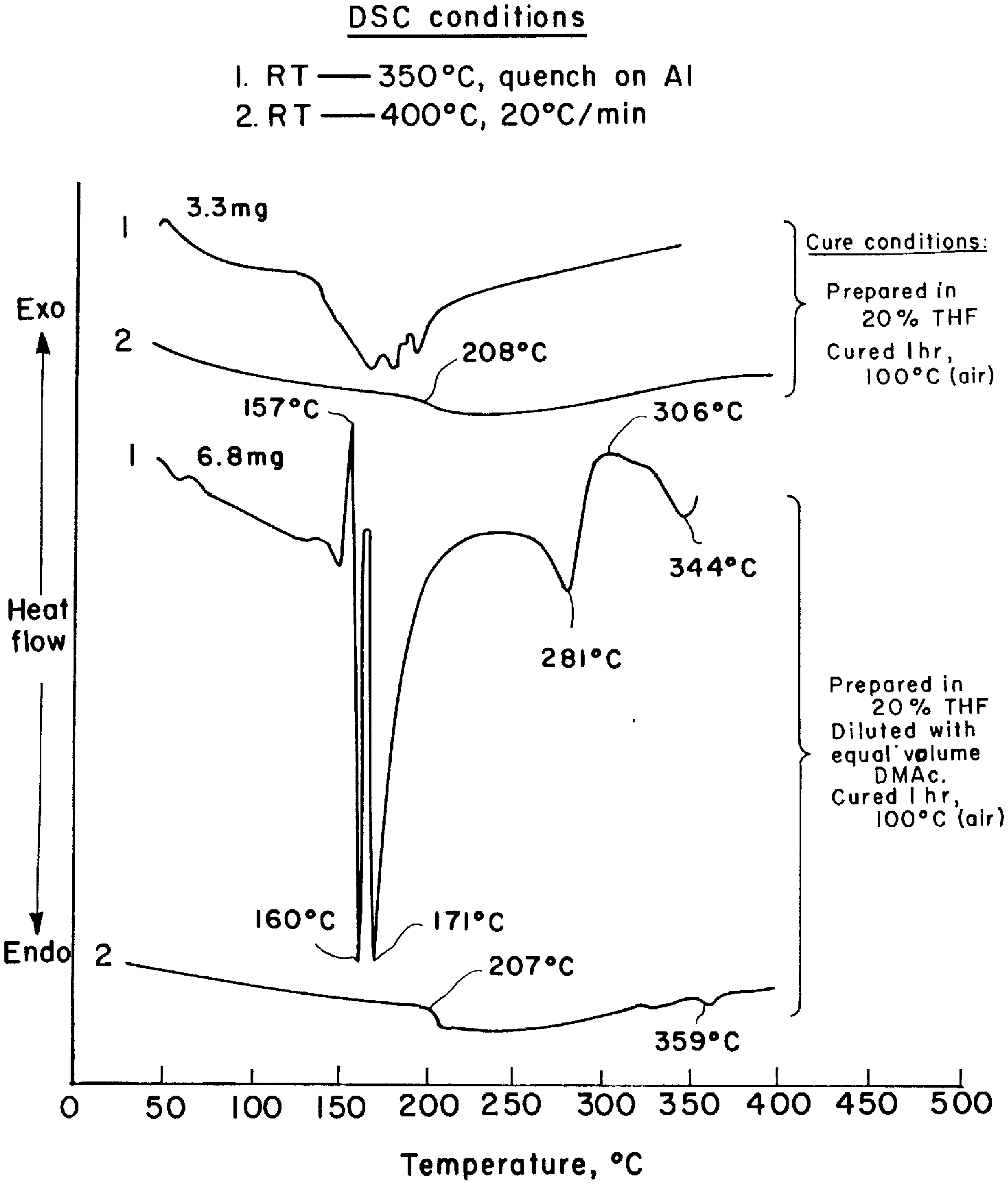

DSC conditions
1. RT —— 350°C, quench on Al
2. RT —— 400°C, 20°C/min
Exo
Heat flow
Endo
1
3.3mg
2
208°C
Cure conditions:
Prepared in 20% THF
Cured 1hr, 100°C (air)
157°C
1
6.8mg
306°C
344°C
281°C
Prepared in 20% THF
Diluted with equal volume DMAc.
Cured 1 hr, 100°C (air)
160°C
171°C
2
207°C
359°C
0
50
100
150
200
250
300
350
400
450
500
Temperature, °C

FIG. 6

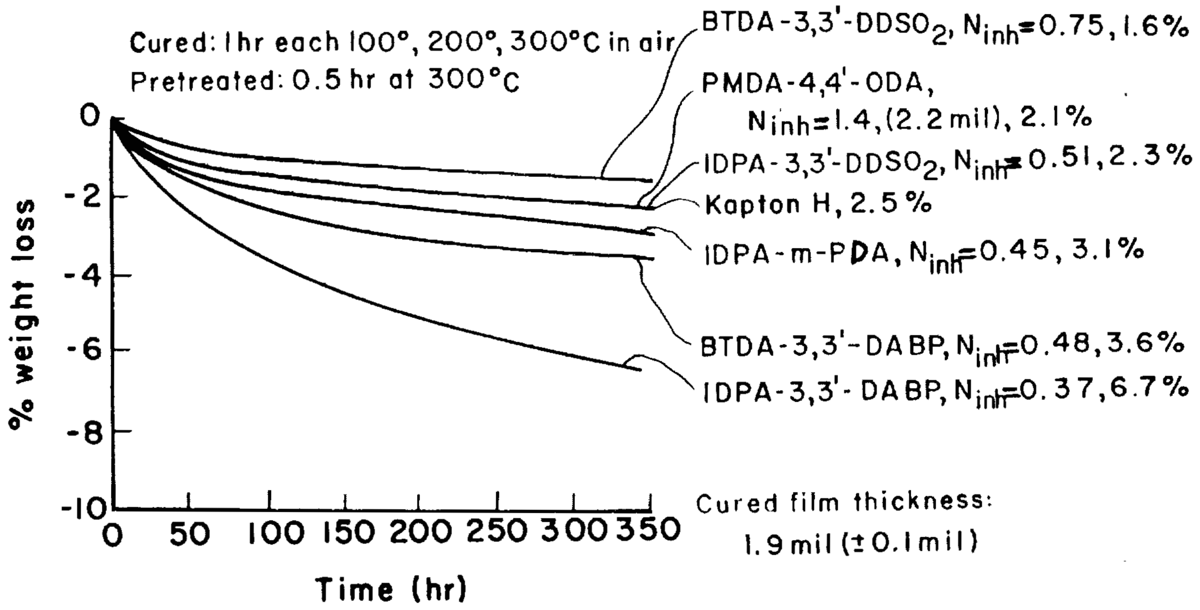

Cured: I hr each 100°, 200°, 300°C in air
Pretreated: 0.5 hr at 300°C
BTDA-3,3'-DDSO$_2$, N$_{inh}$=0.75, 1.6%
PMDA-4,4'-ODA, N$_{inh}$=1.4, (2.2 mil), 2.1%
IDPA-3,3'-DDSO$_2$, N$_{inh}$=0.51, 2.3%
Kapton H, 2.5%
IDPA-m-PDA, N$_{inh}$=0.45, 3.1%
BTDA-3,3'-DABP, N$_{inh}$=0.48, 3.6%
IDPA-3,3'-DABP, N$_{inh}$=0.37, 6.7%
% weight loss
0
-2
-4
-6
-8
-10
0
50
100
150
200
250
300
350
Time (hr)
Cured film thickness:
1.9 mil (±0.1 mil)

FIG. 7

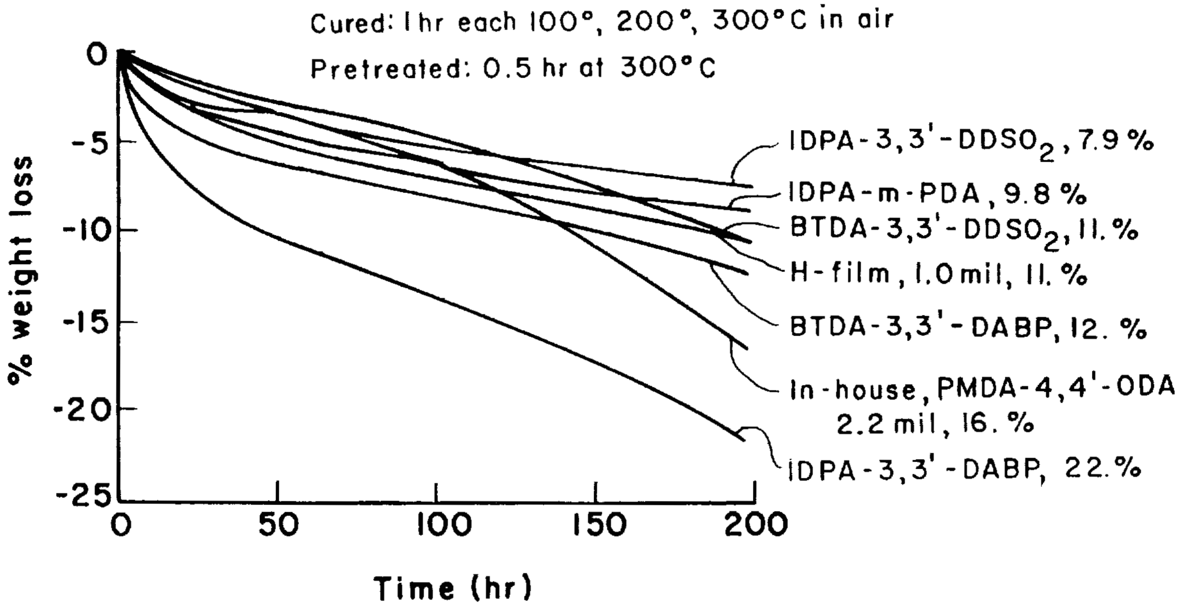

Cured: I hr each 100°, 200°, 300°C in air
Pretreated: 0.5 hr at 300°C
IDPA-3,3'-DDSO$_2$, 7.9%
IDPA-m-PDA, 9.8%
BTDA-3,3'-DDSO$_2$, 11.%
H-film, 1.0 mil, 11.%
BTDA-3,3'-DABP, 12.%
In-house, PMDA-4,4'-ODA 2.2 mil, 16.%
IDPA-3,3'-DABP, 22.%
% weight loss
0
-5
-10
-15
-20
-25
0
50
100
150
200
Time (hr)

FIG. 8

tnn

NOVEL POLYIMIDE COMPOSITIONS BASED ON 4,4'-ISOPHTHALOYLDIPHTHALIC ANHYDRIDE (IDPA)

Origin of the Invention

The invention described herein was made in the performance of work under a NASA Contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, as amended, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

Background of the Invention

1. Field of the Invention

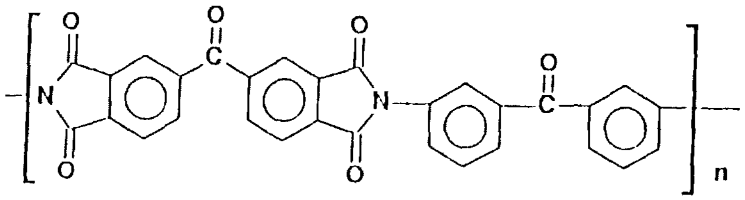
This invention relates generally to polyimides, and in particular to polyimide compositions based on 4,4'-isophthaloyldiphthalic anhydride.

2. Description of Related Art

Polyimides have become preeminent as technologically and commercially viable materials for thermally stable heteroaromatic applications due to their versatility, processability and high level of thermooxidative stability. A large number of new compositions are appearing in the patent literature each year. Examples include high performance polyimide adhesives, which are used in the aerospace industry, for example, in joining metals to metals or metals to composite structures. In addition they are rapidly finding new uses as matrix resins for composites, molding powders, and films. These materials display a number of performance characteristics such as high temperature and solvent resistance, improved flow for better wetting and bonding, solvent resistance, high modulus, chemical and hot water resistance, etc. One area of application is in the manufacture of lighter and stronger aircraft and spacecraft structures.

LaRC-TPI is a thermoplastic polyimide well known as a high performance material (V. L. Bell, B. L. Stump, and H. Gager, J. Polym. Sci., Poly. Chem., Ed. 14, 2275 (1976); D. R. Progar, V. L. Bell, and T. L. St. Clair, NASA Langley Research Center, "Polyimide Adhesives," U.S. Patent No. 4,065,345 (1977); V. L. Bell, NASA Langley Research Center, "Process for Preparing Thermoplastic Aromatic Polyimides," U.S. Patent No. 4,094, 862 (1978); A. K. St. Clair and T. L. St. Clair, NASA Langley Research Center, "High Temperature Polyimide Film Laminates and Process for Preparation Thereof," U.S. Patent No. 4,543,295 (1985); A. K. St. Clair and T. L. St. Clair, "A Multi-Purpose Thermoplastic Polyimide," SAMPE Quarterly, October 1981, pp. 20-25).

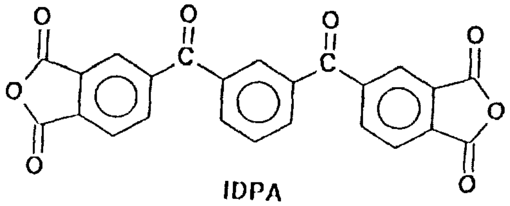
Its structure, as shown below,



LARC-TPI

is derived from 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 3,3'-diaminobenzophenone (3,3'-DABP) and is prepared in 2-methoxyethyl ether (diglyme). It was invented at NASA Langley Research Center and is a commercially available product sold by Mitsui Toatsu (Mitsui Toatsu Chemicals, Inc., New York) and the Rogers Corporation (D. C. Sherman, C. Y. Chen, and J. L. Cercena, SAMPE Preprints, 33, 134 (1988)) as a molding powder, poly(amic acid) solution, and film.

Limited information about 4,4'-isophthaloyldiphthalic anhydride (IDPA) is



IDPA

available. French patent 1,601,094 (September, 1970) deals with the synthesis of this monomer and a recent German patent application (J. Pfeifer, Ciba-Geigy A. G., European patent application, EP 162,017 (November 1985) dealing with the use of IDPA and other aromatic ketoanhydrides in preparing polyimide protective coatings and UV curable photoresists.

A search of IDPA compositions resolved only one citation (J. Pfeifer (Ciba-Geigy A.G.) European Patent Appl. EP 162,017 (November, 1985). This patent application deals with IDPA polyimide compositions containing methylated diamines which undergo crosslinking in the presence of a UV lamp to form a network polymer useful in semiconductor technology.

Historically, polyimides have been regarded as an amorphous class of high temperature polymers. However, the synthesis of new polyimide monomers having certain longer connecting groups between the diamine and dianhydride termini has led to the appearance of a new class of high performance materials called semicrystalline polyimides by dilution of the rigid imide ring. Some of these new polyimide monomers contain aromatic ketone and ether groups similar to those incorporated in semicrystalline polymers like polyetheretherketone (PEEK) or polyetherketoneketone (PEKK) J. F. Carpenter, SAMPE Journal, 24 (1), 36 (1988). Several examples of wholly aromatic, semicrystalline polyimides have appeared (See reference (P. M. Hergenrother, N. T. Wakelyn and S. J. Havens, "Polyimides Containing Carbonyl and Ether Connecting Groups," J. Poly. Sci.: Part A: Poly. Chemistry, Vol. 25, 1093 (1987) and others contained therein).

Crystalline LaRC-TPI is another example of a semicrystalline polyimide which has been developed. This material was prepared by chemically imidizing the poly(amic acid) sequentially with triethylamine and acetic anhydride, T. L. St. Clair, H. D. Burks, N. T. Wakelyn, and T-H. Hou, "Characterization of Crystalline Polyimide LaRC-TPI," Polymer Preprints, 28(1), 90 (1987).

Several potential benefits for developing semicrystalline polyimides include enhanced solvent and caustic chemical resistance, higher tensile strength and modulus, enhanced thermooxidative stability below the melting point and enhanced melt processability, especially when heated to the melting point.

Summary of the Invention

Accordingly, an object of this invention is the preparation of highly thermooxidatively stable, solvent resistant polyimide compositions based on 4,4'-isophthaloyldiphthalic anhydride (IDPA).

Another object of this invention is to produce IDPA compositions that are semicrystalline by Differential Scanning Calorimetry (DSC) or Wide Angle X-ray Scattering (WAXS) in the approximate range of 0 to 25 ±3.5% by use of the proper amide solvent such as N,N-dimethylacetamide (DMAc) and other time/temperature variables.

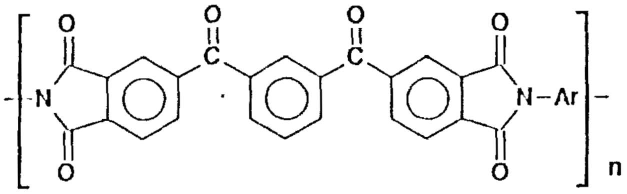
Another object of this invention is the development of two different types of crystallinity by varying the thermal cure conditions to afford a kinetic (lower melting) or a thermodynamic (higher melting) type of semicrystallinity.

Another object of this invention is the preparation of defect-free coatings by curing poly(amic acid) solutions on a substrate, grossly removing the solvent by evaporation in a clean environment, and curing the resulting film to achieve the desired properties.

Another object of this invention is to prepare creasable, high temperature films by casting a poly(amic acid) solution on a substrate, drying in a low humidity environment, and imidizing the film at some elevated temperature.

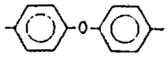
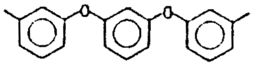
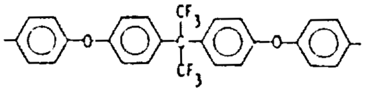
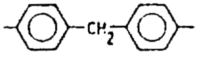
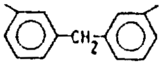
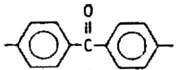
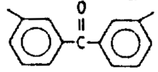
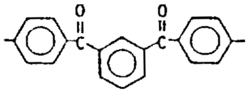
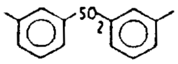
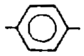
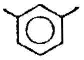
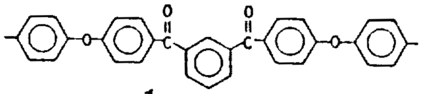
Another object of this invention is to produce the IDPA monomer directly from the corresponding tetracarboxylic acid in pure form by a slurry process in acetic anhydride and cosolvent, thus avoiding time consuming and expensive recrystallization procedures typically encountered.

The present invention relates to a series of high temperature, high performance, linear thermoplastic polyimide compositions. The general structure of these polyimides, based on 4,4'-isophthaloyldiphthalic anhydride (IDPA), is:



where Ar consists of those radicals as shown in Table I derived from the corresponding diamines. Those IDPA polyimides typically give high molecular weight materials; films cast from N,N-dimethylacetamide (DMAc) are usually creasable, lightly colored and have Tgs in the 188-303°C range as determined by differential scanning calorimetry (DSC). They are all insoluble in hot, highly polar solvents like m-cresol and DMAc after a 300°C cure in air.· Their long term thermooxidative stability was found to be excellent at 300°C and 350°C in air. Several compositions were found to be semicrystalline by DSC and wide angle X-ray scattering (WAXS).

Table I
PROPERTIES OF POLYIMIDES BASED ON 4,4'-ISOPHTHALOYLDIPHTHALIC ANHYDRIDE (IDPA)

Ar/Acronym	η_{inh}[1] (dl/g)	Film nature[2]	Tg(°C)	Crystallinity by DSC	Crystalline by WAXS
 4,4'-ODA	0.71	Creasable	240	None	
 m-APB	0.44	Creasable	188	None	NO
 4-BDAF	0.61	Creasable	224	Non-significant	
 4,4'-MDA	0.56	Creasable	246	Non-significant	
 3,3'-MDA	0.96	Creasable	225	Non-significant	
 4,4'-DABP	0.44	Brittle	220	None	
 3,3'-DABP	0.76	Creasable	230	None	
 1,3-BABB'	0.32	Brittle pieces	215	m.p.363°C	Yes
 3,3'-DDSO$_2$	0.51	Brittle	243	None	No(Yes)[3]
 p-PDA	0.92	Brittle pieces	208[4] (303)[5]	Yes	Yes
 m-PDA	0.45	Creasable	259	Non-significant	
 1,3-BABB	1.1	Creasable	213	285°C(endo); 320°C(exo), 350°C(endo)	Yes

[1] Poly(amic acid), DMAC, 35°C
[2] After cure 1 h each 100°, 200°, 300°C in air
[3] Low level after further treatment, 1 h, 325°C
[4] Second order transition
[5] By TBA

Brief Description of the Drawings

For a more complete understanding of the present invention, including its objects and benefits, reference should be made to the Description of the Preferred Embodiments, which is set forth below. This Description should be read together with the accompanying Drawings, wherein:

FIG. 1 is a plot showing differential scanning calorimetry (DSC) transitions of IDPA-1,3-BABB films as cured;

FIG. 2 is a plot showing DSC scans of IDPA-1,3-BABB film treated under various conditions;

FIG. 3 is a plot of compared diffraction intensities v. diffraction angle (2Θ) of IDPA-1,3-BABB films;

FIG. 4 is a plot showing the variation in percent crystallinity of IDPA-1,3-BABB films as a function of final cure temperature for one hour;

FIG. 5 is a plot of dimension change v. temperature of IDPA-1,3-BABB poly(amic acid) film during imidization;

FIG. 6 shows DSC scans revealing the effect of imidization solvent on DSC crystallization;

FIG. 7 shows the isothermal thermogravimetric analysis (ITGA) at 300°C in air; and

FIG. 8 shows the isothermal thermogravimetric analysis (ITGA) at 350°C in air.

Description of the Preferred Embodiments

As shown in FIG. 1, as one cures a poly(amic acid) of IDPA-1,3-BABB from one hour at 100°C (air) (A) to A + one hour, 300°C (air), one hour 350°C (vacuum) (H), this material passes through a series of melting and crystallization transitions at the approximate following temperatures: 180°C (exo, kinetic crystallization); 286°C (endo, kinetic melting); 315°C (exo, thermodynamic crystallization); 348°C (thermodynamic melting). In FIG. 2 one sees (C) that on heating a previously 300°C air cured polyimide to 400°C and slowly cooling in an attempted crystallization, only the amorphous polyimide remains. This change in crystalline structure as a function of cure temperatures was confirmed by WAXS analysis for a series of IDPA-1,3-BABB films (FIG. 3). Thus, the novelty in FIG. 1 is the finding that this polyimide composition has two distinct melting and crystallization temperatures each and hence two distinct types of crystallinity. This observation was confirmed visually, as all films cured above 125°C were translucent and creasable. Polarized light microscopy revealed spherulitic structures in some of the films 6-8μ±0.5μ in diameter having the familiar Maltese cross patterns. Hence, there exists, in concept, a new method for developing multiple crystallinity forms in IDPA, linear aromatic polyimides.

A crystalline mapping experiment of IDPA-1,3-BABB composition (FIG. 4) shows that a linear increase in crystallinity with increasing cure temperature does not exist for this polyimide. Rather, the maximum percent crystallinity exists after a cure for one hour each at 100°, 200° and 275°C in air. One can thus control the percent crystallinity in this IDPA-1,3-BABB film by controlling the final curing temperature.

The existence of the two types of crystalline melting transitions is further illustrated in FIG. 5. Here, melting at 295° and 391°C corresponding to kinetic and thermodynamic transitions are shown by thermomechanical (TMA) stretching of a thin film under tension. The initial stretching at 157°C is associated with imidization of the poly(amic acid) film.

The importance of solvent choice in controlling the degree of crystallinity is further illustrated in FIG. 6. As previously shown, an IDPA-1,3-BABB poly(amic acid) film containing DMAc, when cured, is semicrystalline to a degree depending on the time/temperature of this cure. A similar film prepared and cast from tetrahydrofuran (THF) and cured one hour at 100°C in an air oven and then further heated to 400°C in a DSC cell showed no crystallization and melting transitions, although a Tg of 208°C was found. Furthermore, when the THF poly(amic acid) solution was diluted with an equal volume of DMAc and a dried film prepared and cured to 100°C for one hour, the DSC run to 400°C showed the multiple melting and crystallization transitions. It is therefore readily apparent that amide solvents like DMAc play a major role in inducing crystallization in certain polyimides. This phenomenon of solvent induced crystallization now reported here for polyimides is unexpected.

Table II presents tensile properties of an IDPA-1,3-BABB film cured to 275°C and 325°C (respective maxima in the percent crystallinity map for the kinetic and thermodynamic spherulite forms). As can be seen, respectable yield strengths, tensile strengths, tangent moduli, and percent elongation were obtained at both 25°C and 200°C test temperatures.

Air imidization conditions	Stress temperature (°C)	Average yield strength• (psi)	Average tensile strength• (psi)	Average tangent modulus• (x 10^6 psi)	Average % elongation•
1 h each 100°, 200°, 275°C	25	12,200^{-} (11,600-13,300)	16,700^{-} (14,900-18,400)	0.590^{-} (0.533-0.694)	3.7^{-} (3.3-4.7)
"	200	6,210 (6,000-6440)	7,980 (7,500-8560)	0.402 (0.370-0.461)	7.5 (3.0-14)
1 h each 100°, 200°, 325°C	25	12,300^{-} (11,600-13,100)	17,400^{-} (16,500-18,300)	0.539^{-} (0.519-0.554)	4.1^{-} (3.7-4.4)
"	200	6,290 (5,560-6,390)	7,030 (6,630-7,650)	0.408 (0.344-0.466)	12. (9.3-17)

Nominal 2 mil films

• Values in parenthesis represent range.

$^{-}$Average of 4 values

Table II. Film tensile properties of the IDPA-1,3-BABB polyimide cured to 275°C and 325°C in air. (Average of five values for each specimen unless otherwise noted).

The isothermal thermooxidative stabilities as determined by isothermal thermogravimetric analysis (ITGA) at 300°C (FIG. 7) and 350°C (FIG. 8) in ambient air of the IDPA polyimides are excellent. Weight loss at 300°C after 350 hours for IDPA compositions with 3,3'-$DDSO_2$, m-PDA and 3,3'-DABP were 2.3, 3.1 and 6.7% respectively, compared to Kapton H® film (du Pont) which lost 2.5%. Similarly, after 200 hours at 350°C the same IDPA compositions had lost 7.9%, 9.8% and 22% while Kapton H® film had lost 11% weight of decomposition.

The synthesis of IDPA monomer known in the art has a final cyclization step of the diketotetracarboxylic acid to IDPA which involves dissolving the crude tetracarboxylic acid in acetic anhydride at 8-10°C, filtering rapidly at this temperature, and warming to 30°C. The IDPA precipitates and is then washed with acetic acid and dried to give IDPA, mp. 218°C in 80% yield.

The instant method of cyclization, on the other hand, consists of slurrying the IDPA tetracarboxylic acid (or partially cyclized anhydrides formed during drying in the previous step) with refluxing acetic anhydride and cosolvent such as glacial acetic acid or toluene. Both reactant and product remain suspended in the media as a slurry as the IDPA is formed; impurities remain dissolved and are filtered hot leaving the product IDPA behind. Vacuum drying affords polymer grade IDPA in 91%.

This slurry process is novel in that recrystallization of the IDPA from common organic solvents such as xylenes, toluene, or acetone is unnecessary. Such a recrystallization step, if used, is impractical because of the low solubility of IDPA in most common organic solvents.

EXAMPLES

Example I

The reaction of 4,4'-oxydianiline (4,4'-ODA) (0.1879 g, 9.38×10^{-4} mol) with 4,4'-isophthaloyldiphthalic anhydride (IDPA) (0.4000 g, 9.38×10^{-4} mol) in 2.3514g N,N-dimethylacetamide (DMAc) to give a solution of 20% solids overnight afforded a poly(amic acid) solution of inherent viscosity (η_{inh}) of 0.71 dl/g (35°C, in DMAc). A nominal 20 mil film was cast onto glass, and much of the DMAc was allowed to evaporate in a clean box overnight. This film was cured for one hour each at 100°, 200°, and 300°C in a forced air oven. The resulting creasable film (thickness 1.8 mil) had a glass transition temperature, Tg, of 240°C as measured by differential scanning calorimetry (DSC) and displayed no other transitions up to 450°C.

Example II

The reaction of 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) (0.3648g, 7.04 x 10^{-4} mol) with IDPA (0.3000g, 7.04 x 10^{-4} mol) in 2.6596g (20%) DMAc as in Example I afforded a poly(amic acid) solution with an inherent viscosity of 0.61 dl/g at 35°C in DMAc. A yellow, creasable film 1.9 mils in thickness was obtained by curing a dried poly(amic acid) film in air one hour each at 100°C, 200°C and 300°C in air. The Tg by DSC was 224°C and displayed a small endotherm at 477°C.

Example III

The reaction of IDPA (0.2000g, 4.691 x 10^{-4} mol) with 3,3'-diaminobenzophenone (3,3'-DABP) (0.09957g, 4.691 x 10^{-4} mol) in 1.1983g DMAc (20% solution) overnight as in Example I at 25°C afforded a poly(amic acid) of inherent viscosity of 0.37 dl/g. A moderately brittle film with a Tg of 224°C was obtained when the poly(amic acid) film was cured to 300°C in air. The DSC showed an essentially amorphous film having a small endotherm at 437°C.

Example IV

The reaction of IDPA and 4,4'-diaminobenzophenone (4,4'-DABP) in 20% DMAc as in Example I afforded a poly(amic acid) solution with an inherent viscosity of 0.44 dl/g. A nominal 20 mil film was cast on glass, dried in a clean box and cured to 300°C in air. The resulting 1.5 mil moderately brittle film had a Tg of 220°C (DSC) and gave no indication of semicrystallinity by DSC up to 550°C.

Example V

The reaction of IDPA and 3,3'-diaminodiphenylsulfone (3,3'-DDSO$_2$) in 20% 2-methoxyethyl ether (diglyme) as in Example I afforded a poly(amic acid) solution with an inherent viscosity of 0.51 dl/g. The resulting 300°C air cured film was brittle and snapped on attempted creasing. The DSC Tg was 243°C, and the polyimide appeared to be amorphous.

Example VI

The reaction of IDPA and 3,3'-diaminodiphenylmethane (3,3'-MDA) as in Example I afforded a poly(amic acid) solution with an inherent viscosity of 0.96 dl/g. The film cured to 300°C in air was creasable and had a Tg of 225°C (DSC) as well as a small endotherm at 522°C.

Example VII

The reaction of IDPA and 4,4'-diaminodiphenylmethane (4,4'-MDA) as in Example I afforded a poly(amic acid) solution with an inherent viscosity of 0.56 dl/g. A film cured to 300°C in air was creasable and displayed a Tg of 246°C as well as a small endotherm at 450°C by DSC.

Example VIII

The reaction of IDPA and p-phenylenediamine (p-PDA) as in Example I gave a poly(amic acid) with an inherent viscosity of 0.92 dl/g. A film cured to 300°C in air resulted in many brittle pieces of film with second order transition at 208°C and a broad DSC exotherm at 497°C, followed by a sharp endotherm at 523°C. The pieces of film were semicrystalline when examined by wide-angle X-ray scattering (WAXS). The torsional braid analysis spectrum gave a Tg of 300°C on heat-up, based on the change in the relative rigidity and a transition at 306°C based on the damping index. No transitions were seen in cool-down to 25°C.

Example IX

The reaction of IDPA and 1,3-bis(4-aminobenzoyl)benzene(1,3-BABB') as in Example I gave a poly(amic acid) solution with an inherent viscosity of 0.32 dl/g. The 300°C cured film consisted of brittle film pieces having a Tg of 215°C and a DSC melting endotherm of 363°C. The film pieces showed semicrystalline patterns by WAXS.

Example X

The reaction of IDPA and 1,3-bis(3-aminophenoxy)benzene (m-APB) as in Example 1 afforded a poly(amic acid) with an inherent viscosity of 0.44 dl/g in DMAc at 35°C. A 20 mil wet cast poly(amic acid) film was cured in air to 300°C. The resulting polyimide film was creasable, had a Tg of 188°C, and displayed no semicrystallinity by DSC or WAXS.

Example XI

The reaction of IDPA and 1,3-bis(4-aminophenoxy-4'-benzoyl)-benzene(1,3-BABB) in 20% DMAc as in Example I formed a poly(amic acid) of inherent viscosity 1.06 dl/g in DMAc and 35°C. A 20 mil wet thickness film was cast on soda lime glass, dried overnight in a clean box and imidized one hour each at 100°C, 200°C, and 300°C. The resulting creasable polyimide had a Tg of 213°C (DSC) and a final crystalline melting point of 350°C. This crystallinity was confirmed by its WAXS pattern.

DSC assignments were made on a DMAc film dried and cured in air for one hour at 100°C. They were as follows: 170°C (endo) imidization, DMAc and water loss; 195°C (exo) kinetic (solvent induced) crystallization; 285°C (endo) kinetic melting; 320°C (exo) thermodynamic crystallization; and 350°C (endo) thermodynamic melting. Removal of most of the DMAc from the poly(amic acid) film before cure (CH_2Cl_2 extraction) was shown to impede crystallization. The resulting cured polyimide film was thick, porous and amorphous. All polymer films cast from DMAc and cured to or above 125°C were translucent and semicrystalline. At 125°C DSC curing transitions disappeared, the polymer had a second order transition of 175°C, and three first order transitions remained. At cure temperatures greater than 287°C only a thermodynamic melting transition remained. Transmission polarized light microscopy indicated the presence of crystalline spherulites after curing films to 250°C and 275°C. No spherulites were detected in films cured at other temperatures. WAXS data (Hermans-Weidinger method) indicated that the polyimide had a maximum crystallinity of 25°±3.5%.

Example XII

Preparation of IDPA by a Novel Slurry Process. A mixture of 170 g of the tetracarboxylic acid of IDPA as obtained from the nitric acid oxidation step (no doubt containing some IDPA and mixed anhydride - orthodicarboxylic acid), 200 ml acetic anhydride and 100 ml glacial acetic acid was heated at reflux for three hours. Little material appeared to dissolve. The product was then filtered while hot through a coarse sintered glass funnel and was rinsed with 500 ml of hot acetic anhydride-acetic acid (1:1). The snow white IDPA powder was then vacuum dried at 195°C for over four hours. The yield was 128g of high purity IDPA, m.p. (sharp DTA maximum), 216°C. A second crop crystallized from the filtrate at room temperature to afford 21.1g of impure IDPA which was discarded.

The present invention has been described in detail with respect to certain preferred embodiments thereof. As is understood by those of skill in the art, variations and modifications in this detail may be made without any departure from the spirit and scope of the present invention, as defined in the hereto-appended claims.

What is claimed is:

NOVEL POLYIMIDE COMPOSITIONS BASED ON 4,4'-ISOPHTHALOYLDIPHTHALIC ANHYDRIDE (IDPA)

Abstract of the Disclosure

A series of twelve high temperature, high performance polyimide compositions based on 4,4'-isophthaloyldiphthalic anhydride (IDPA) has been prepared and characterized. Tough, film-forming, organic solvent-insoluble polyimides were obtained. Three materials were semicrystalline. Several gave excellent long-term thermooxidative stability by isothermal thermogravimetric analysis (ITGA) at 300°C and 350°C in air when compared to Kapton H® film (duPont). One extensively studied material displayed different levels of semicrystallinity over a wide range of final cure time/temperatures. The polyimide from IDPA and 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene exhibited multiple crystallization and melting behavior, implying the existence of two kinetic and two thermodynamic crystallization and melting transitions by differential scanning calorimetry (DSC).