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(NASA-Case-LAR-14339-1) A TOUGH PERFORMANCE N90-26955  
SIMULTANEOUS SEMI-INTERPENETRATING POLYMER  
NETWORK Patent Application (NASA) 31 p  
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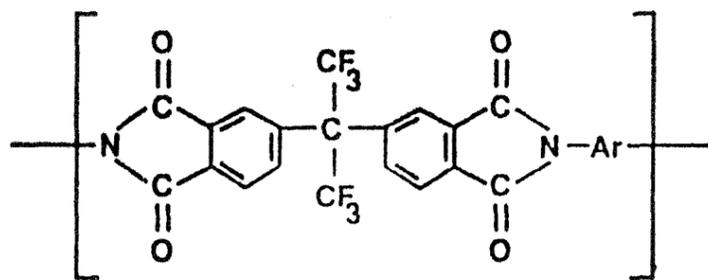
# TOUGH HIGH PERFORMANCE SIMULTANEOUS SEMI-INTERPENETRATING POLYMER NETWORK

## AWARDS ABSTRACT

NASA Case No. LAR 14339-1

There is a continual search in the art for more processable and damage tolerant high temperature polymers for use as moldings, adhesives and composite matrices in aerospace and electronic technologies. Materials used in these environments must have a variety of desired properties including easy processing, good damage tolerance, a high glass transition temperature, good mechanical performance capable of withstanding high temperature, low moisture absorption, and resistance to a variety of organic solvents. Although polymers exist that exhibit one or more of the above properties, these materials are generally deficient in at least one other desired property.

The present invention is a semi-interpenetrating polyimide network and methods for making and using the same are disclosed. The semi-IPN system comprises a high performance thermosetting polyimide having an acetylene-terminated group acting as a crosslinking site and a high performance linear thermoplastic polyimide having the following repeating unit:



The polymer is made by combining low viscosity precursors and low molecular weight polymers of the thermosetting and thermoplastic polyimides and allowing them to react in the immediate presence of each other to form a simultaneous semi-interpenetrating polyimide network.

The novelty of the present invention resides in the provision of a high

temperature system having significantly improved processability and damage tolerance while maintaining excellent thermo-oxidative stability, mechanical properties and resistance to humidity, when compared with the commercial high temperature resin, Thermid 600. This material is particularly adapted for use as a molding, adhesive, and advanced composite matrix for aerospace structural and electronic applications.

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Serial No.: 07/430,470

A TOUGH HIGH PERFORMANCE SIMULTANEOUS  
SEMI-INTERPENETRATING POLYMER NETWORK

Cross-Reference

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This application is related to co-pending patent application serial number \_\_\_\_\_, filed \_\_\_\_\_, entitled A Tough High Performance Composite Matrix.

10 Origin of the Invention

The invention described herein was made by an employee of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

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Background of the Invention

1. Field of Invention

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The present invention relates generally to high temperature polymers. It relates particularly to a semi-interpenetrating polymer network approach to the obtainment of more processable, tougher and more moisture resistant high temperature polymers. The systems are particularly adapted to use as moldings, adhesives and composite matrices.

25

2. Description of the Related Art

There is a continual search in the art for more processable and damage tolerant high temperature polymers for use as moldings, adhesives and composite matrices in aerospace and electronic technologies. Materials used in these environments must have a variety of desired properties including

30

easy processing, good damage tolerance, a high glass transition temperature, good mechanical performance capable of withstanding high temperature, low moisture absorption, and resistance to a variety of organic solvents. Although polymers exist that exhibit one or more of the above properties, 5 these materials are generally deficient in at least one other desired property.

For instance, the well-known and commercially available acetylene-terminated Thermid Polyimide series offers outstanding thermo-oxidative stability, exceptional dielectric properties and excellent resistance to humidity at elevated temperature. It is also addition-curable. 10 However, it is inherently brittle due to its highly crosslinked structure.

Despite having the advantage of addition-curing, this system is actually difficult-to-process. This is primarily due to the fact that this system has a very narrow processing window. (Thermid MC-600, for example, has a gel-time of three minutes at 190°C.) The problem becomes exacerbated when 15 the resin is used to fabricate composites, particularly large area laminated structures.

Conversely, NR-150B2, which is available from E. I. DuPont de Nemours and Company, is well-known for its outstanding toughness and microcracking resistance, in addition to its unusually high thermo-oxidative 20 stability. However, this material also has a major drawback. It is difficult to process and requires a high processing temperature such as 400°C.

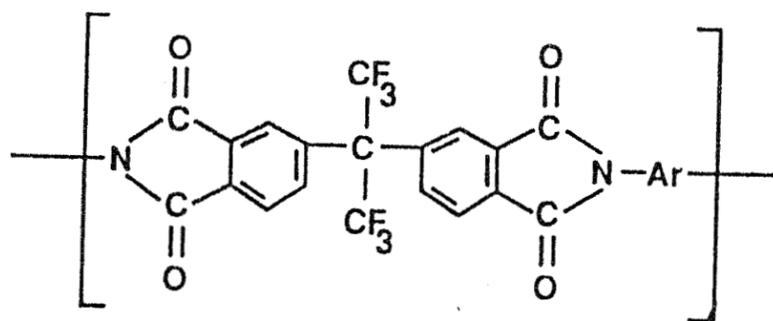
St. Clair et al., (U.S. 4,695,610) and others have developed semi-interpenetrating polymer networks (semi-IPNS) of high temperature systems. However, none of these prior art products have the desired 25 combination of properties set forth hereinabove.

#### Summary of the Invention

Accordingly, a primary object of this invention is to provide an improved 30 high temperature polymer having the combination of easy processing, damage tolerance and excellent moisture resistance. This primary object and other objects and benefits are achieved by making a semi-IPN comprising a

high performance thermosetting polyimide having an acetylene terminated group acting as a crosslink site and a high performance linear thermoplastic polyimide having the following repeating unit:

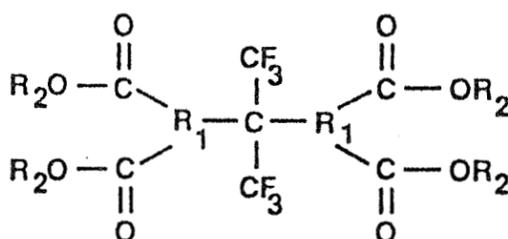
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Especially beneficial results are obtained when the high performance linear thermoplastic polyimide comprises a mixture of the following compounds:

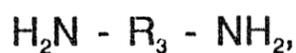
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wherein  $R_1$  is a trivalent aryl radical and  $R_2$  is hydrogen or alkyl; and

25

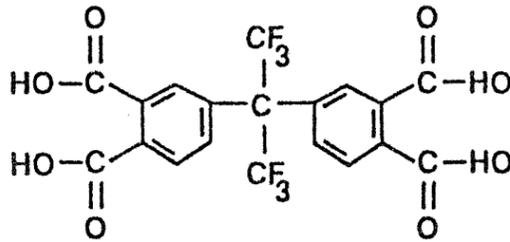


wherein  $R_3$  is a divalent aryl radical.

Excellent results are achieved when the high performance linear thermoplastic polyimide comprises a mixture of the following three compounds:

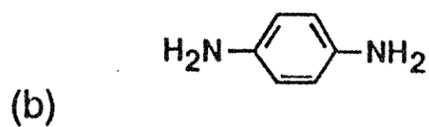
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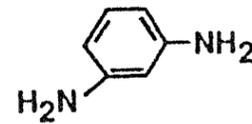
(a)

10



and

(c)



15

especially when compound (a) is present in a stoichiometric quantity, and the molar ratio of compound (b):compound (c) is about 95:5.

A number of additional, especially-preferred embodiments are found in the following Detailed Description of the Invention.

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#### Brief Description of the Drawing

The single Figure is a schematic depiction of a semi-IPN synthesis.

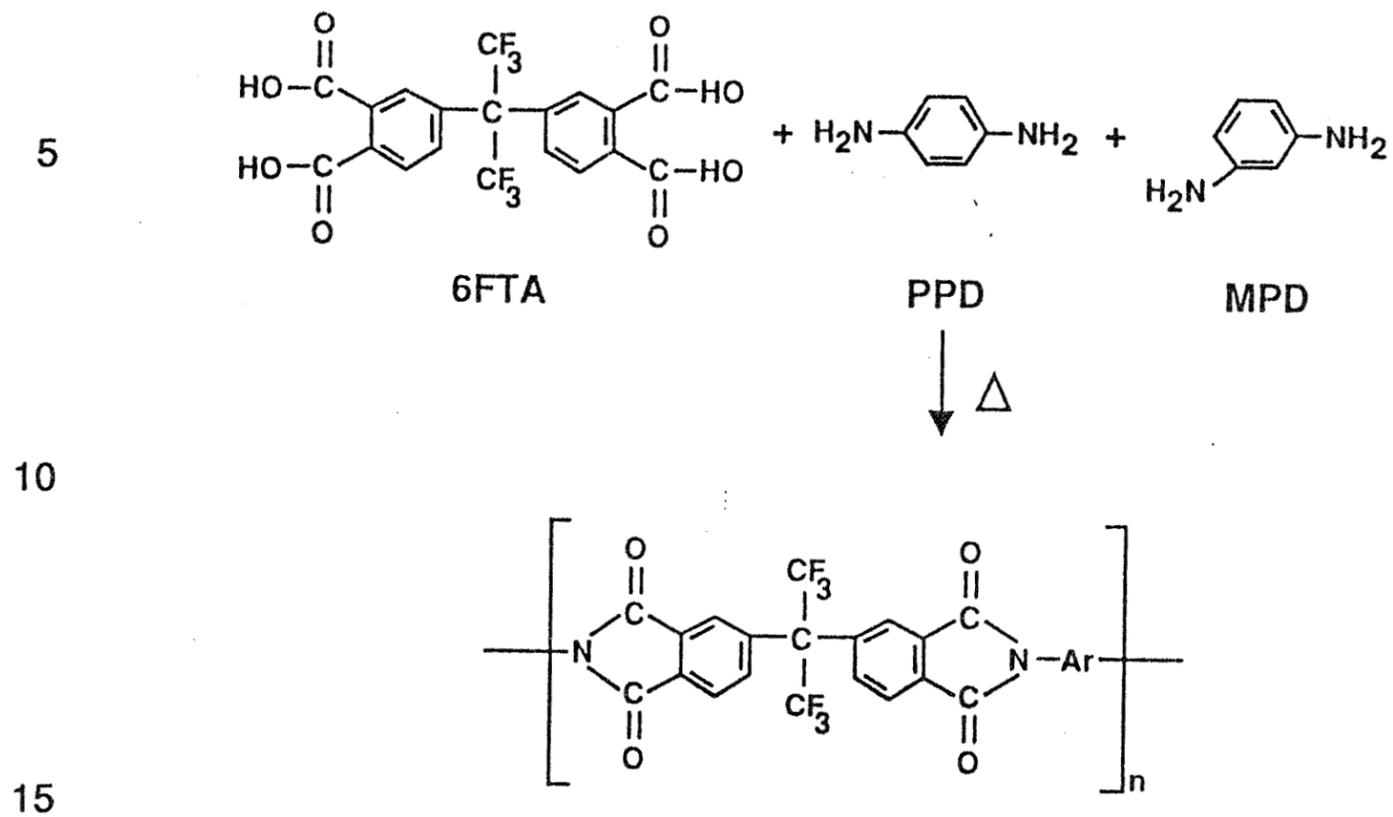
#### 25 Description of the Preferred Embodiments

The concept of the high performance semi-IPN synthesis is shown in the drawing. One or more easy-to-process, but brittle thermosetting polyimides are combined with one or more tough, but difficult-to-process  
30 linear thermoplastic polyimides to form a semi-IPN polyimide having a combination of several desirable properties, including easy processability, damage tolerance, good mechanical performance and good thermo-oxidative

stability. In the present invention, the combination of desired properties is achieved by controlling factors which include (1) careful selection of constituent polymer components, (2) composition variation of the constituent materials, (3) processing parameters and (4) thermodynamic and chemical kinetics variables to control the phase morphology and phase stability. Each of these factors is discussed in detail in the following paragraphs.

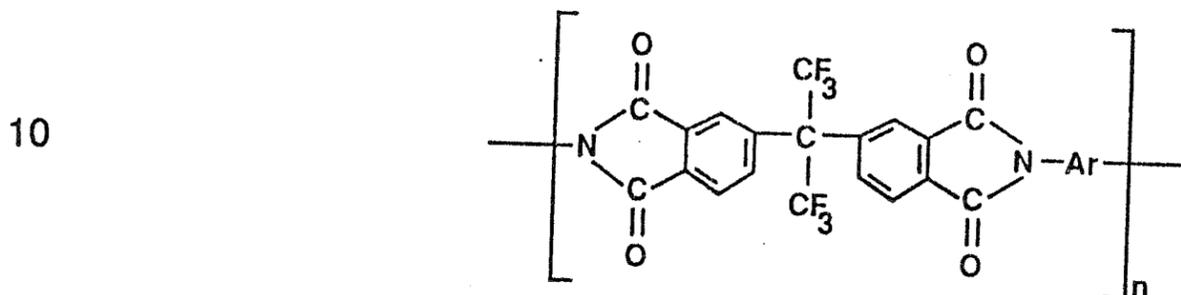
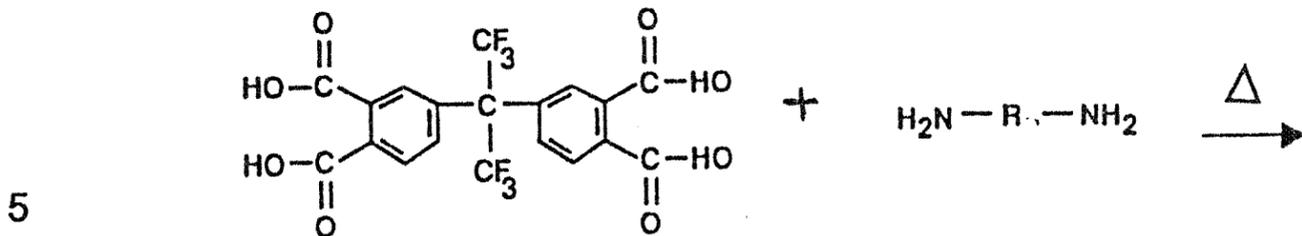
The selection of the constituent thermosetting and thermoplastic polyimides is based primarily on their processing and property compatibility. The processing parameters considered of particular importance are solubility in a common organic solvent and compatible cure cycle. Further, these polymers must have comparable glass transition temperatures ( $\pm 50^\circ\text{C}$ ), mechanical performance, and thermo-oxidative stability.

The semi-IPN of this invention comprises a polyimide which contains an acetylene terminated group acting as a crosslinking site and an NR-150B2 polyimide. The NR-150B2 polyimide precursor solution in N-methylpyrrolidone (NMP) solvent is obtained from E. I. Dupont de Nemours and Company (hereafter Dupont). The polyimide precursor solutions in ethanol solvent under the trademarks NR-150B2 S2X to NR-150B2 S2X10 are also obtained from DuPont. The NR-150B2 polyimide can also be prepared as set forth in U.S 4,3,959,350, according to the following reaction:



## NR-150B2 Polyimide

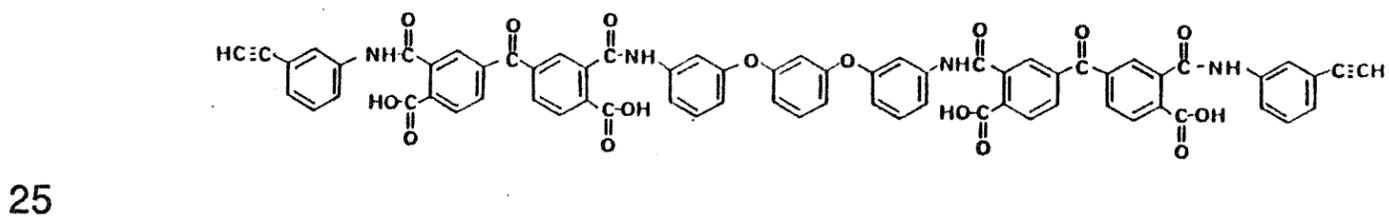
- 20 The linear thermoplastic polyimide prepared from 6FTA and an aromatic diamine or a diamine mixture comprising two or more aromatic diamines according to the following reaction equation has utility to the present invention:



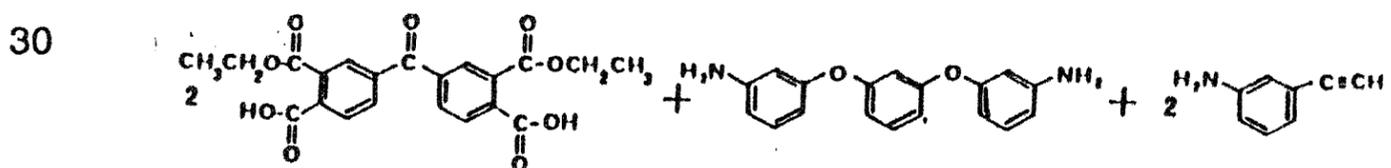
15 wherein R is a divalent aryl radical.

Several thermosetting acetylene-terminated aromatic polyimides are considered compatible with an NR-150B2 polyimide and, therefore, can be used in this invention. These include (1) Thermid LR-600 having the

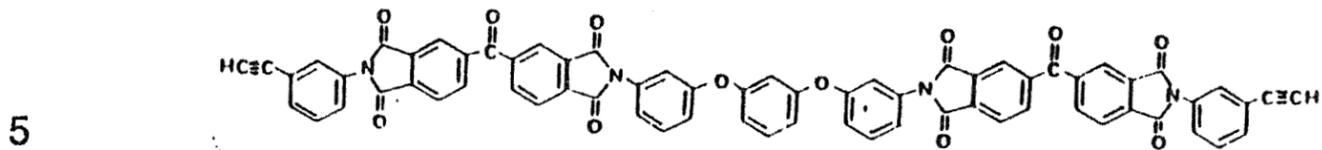
20 following chemical formula:



(2) Thermid AL-600 which comprises the following monomeric precursors:

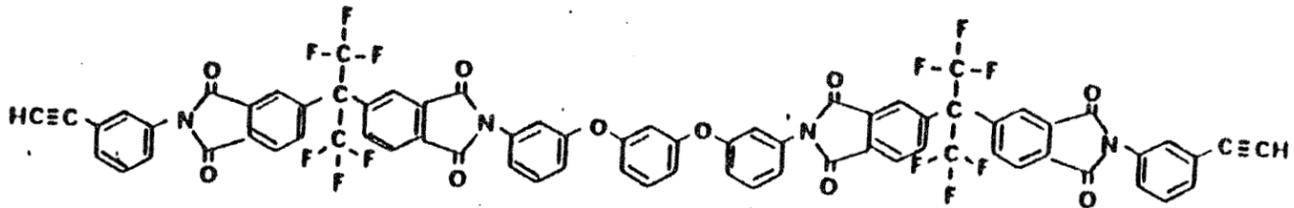


(3) Thermid MC-600 represented by the formula:



(4) Thermid FA-700 having the following formula:

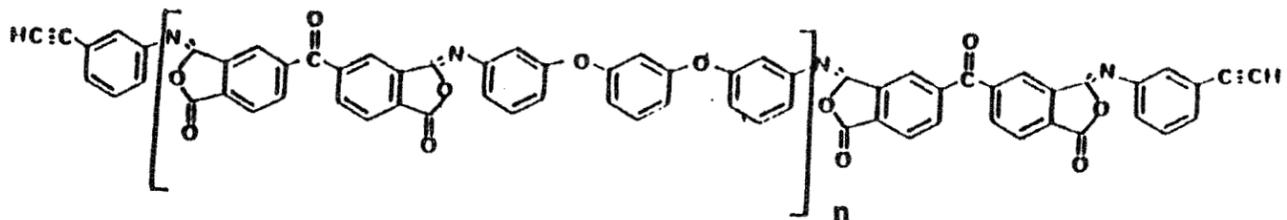
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and finally, Thermid IP-600 which has a general formula shown below:

20



25

wherein  $n = 1$  to 30.

All of the above thermosetting polyimides are commercially available from National Starch and Chemical Corporation (Bridge-  
 30 water, New Jersey).

The composition of the constituent thermosetting and thermoplastic polyimides significantly affects many aspects of the processing, properties

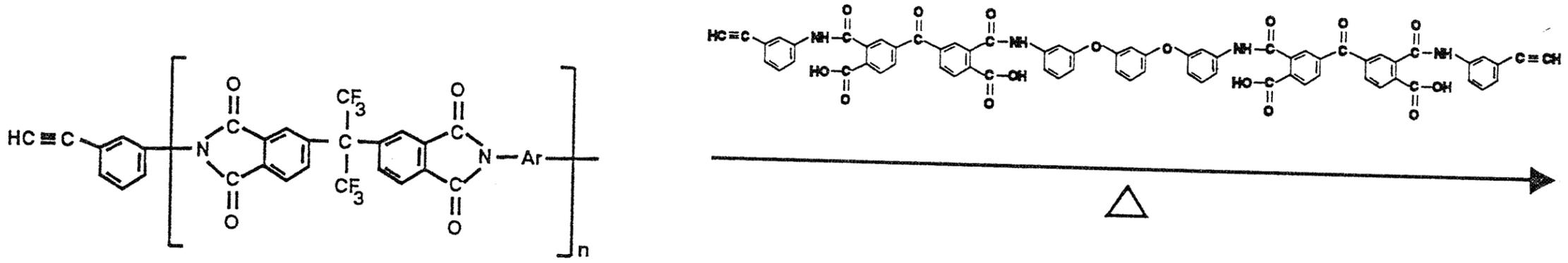
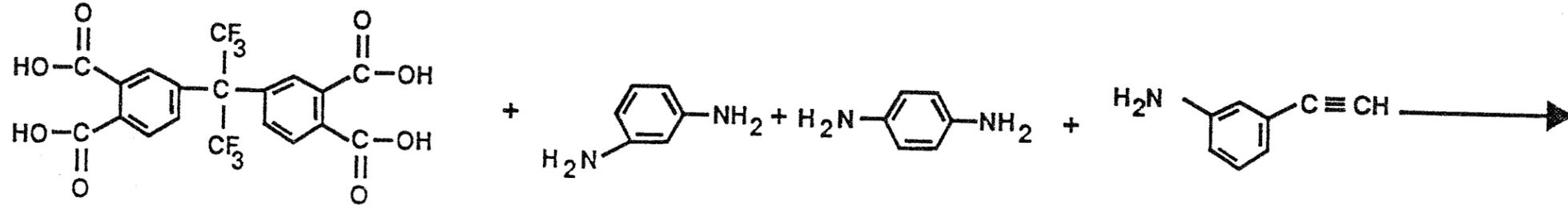
and morphology of the semi-IPN. It has been found that increasing the concentration of the thermoset component increases the processability and performance of the semi-IPN, but at a cost of decreasing toughness characteristics. While the weight ratio of the acetylene-terminated polyimide to NR-150B2 can be varied from 95:5 to 5:95, the ratio between 80:20 to 20:80 is preferred. However, the ratio of 80:20 is particularly preferred because this composition offers the best overall balance of processing, performance and cost effectiveness.

The synthesis of the present semi-IPN can proceed in two major ways: simultaneous and sequential. In the former, the uncrosslinked acetylene-terminated prepolymers are combined with the monomer precursors of the NR-150B2. With application of heat, the acetylene-terminated prepolymers are allowed to crosslink in the immediate presence of the NR-150B2 polyimide undergoing simultaneous linear chain extension. This synthesis can lead to a network in which one polymer interlocks with the other, forming permanent entanglements at the interfacial regions of the two polymer systems. The resulting physical crosslinking provides synergistic properties. This synthesis is designed so that the constituent polymers are formed independently without any chemical interference between the precursors of the thermosetting and thermoplastic polyimides. The sequential method involves a process in which one polymer is synthesized and/or crosslinked in the immediate presence of the other which has been prepolymerized. There are two sequential semi-IPNs: semi-1-IPN and semi-2-IPN. The former is prepared by polymerizing a linear polymer in a precrosslinked network. The reverse sequence results in a semi-2-IPN. In this invention, the simultaneous method is preferred, because it offers easier processing, better performance and less phase separation, as compared with the sequential approach. There is yet another synthetic method which is non-conventional. This method involves mixing the monomers of the thermosetting component with the monomers of the thermoplastic component and allowing the monomers to react randomly to form a simultaneous semi-IPN. The inter-reaction between monomers of the thermoset and

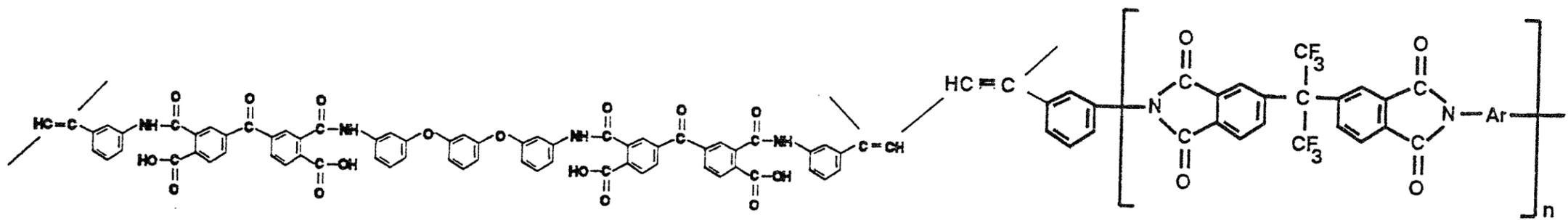
thermoplastic occurs, which results in a semi-IPN significantly different in chemical structure and properties from those prepared by the previous methods.

As discussed earlier, one of the disadvantages of the Thermid system is that it exhibits an extremely small processing window. The problem is unexpectedly resolved by the present semi-IPN synthesis for the following reason. According to a proposed mechanism, the polymerization proceeds via a free radical propagation of an acetylene group to form a linear conjugated polyene, which then acts as a crosslink site for the subsequent crosslinking reaction. The curing reaction is extremely sensitive to any steric hinderance surrounding the reaction sites. When a long polymeric chain (NR-150B2) is in the immediate vicinity of the crosslink site, as in the case of the present semi-IPN synthesis, the kinetics of the acetylene reaction is expected to slow down considerably, thus, broadening the processing window. Consequently, the semi-IPN of the present invention exhibits improved processability over the Thermid material. For a different reason, the present semi-IPN system is also anticipated to have easier processing compared to the pure NR-150B2. The Thermid material has excessive flow whereas the NR-150B2 system exhibits limited flow. The combination would then provide a material having a flow intermediate between the constituent polymer systems.

A method to control the phase morphology and phase stability has been investigated. It involves the addition of 0.1 to 5 weight percent of 3-aminophenyl acetylene into the NR-150B2 monomer precursors. To this mixture the preimidized acetylene-terminated prepolymers are added. The concept involves lightly end-capping the NR-150B2 with an acetylene group to form an acetylene end-capped NR-150B2 polyimide. Through the common acetylene end group, the acetylene end-capped NR-150B2 is then crosslinked with the acetylene-terminated polyimide to give a graft copolymer upon heating. An example of this synthesis is shown below.



Acetylene-capped NR150B2



Graft copolymer

Because of chemical bonding between the constituent polymers, the resultant graft copolymer exhibits less phase separation and better long term phase stability, as compared with the physically crosslinked semi-IPNs prepared by the previous methods.

5 The semi-IPN polyimide of this invention for adapted to use as a composite matrix, and as an adhesive and molding compound for long-term applications in the 200°C to 316°C in aerospace structural components, especially in electronic technologies.

10 The following are examples that illustrate preparation and use of the semi-IPNs for applications in advanced composites, structural adhesives and molding articles. However, it is to be understood that the examples are merely illustrative and intended to enable those skilled in the art to practice the invention in all of the embodiments flowing therefrom, and do not in any way limit the scope of the invention as defined in the claims.

15

## EXAMPLES

### Example 1

#### 20 Preparation of Semi-IPN of Thermid LR-600 and NR-150B2

This semi-IPN was prepared by the simultaneous synthetic method generally described previously. In this synthesis, an acetylene-terminated polyimide crosslinks in the immediate presence of an NR-150B2 polyimide undergoing simultaneous linear chain extension to afford a simultaneous  
25 semi-IPN. It is possible that transimidization reaction occurs between the amic acid of the Thermid system and the monomer precursors of the NR-150B2 material. This would result in a material somewhat similar to the material prepared in Example 2 but different from that made in Example 3. Thus, it is of interest to compare their properties. Such a synthesis is  
30 described in the following. To 104.0 g of a Thermid LR-600 solution (50 percent by weight of an amic acid in NMP) was added 27.0 g of an NR-150B2 monomer precursor solution (48 percent solid content in NMP) and

45.0 g of freshly distilled NMP. This mixture was stirred at room temperature for one hour, resulting in a viscous dark brown solution containing about 37 weight percent solids in which the Thermid LR-600 amic acid and NR-150B2 monomeric materials were present in 80 and 20 weight percent, respectively.

- 5 For a molding application, the solution was poured into distilled water and blended using a mechanical blender. The precipitated solids were filtered, dried at 100°C for two hours under vacuum and staged at 204°C for one-half hours to afford a black molding powder. About 15.61 g of the molding powder was compression molded at 250°C for one hour and at  
10 316°C for another hour under 2500 psi pressure, and then removed from the press when the mold temperature reached 177°C. This gave a neat resin having dimensions of 3.2 cm by 3.2 cm by 1.0 cm and a density of 1.34 g/cc. The surfaces of the neat resin showed no voids, cracks or defects, and thus it was accepted for compact tension specimen preparation without  
15 further post curing. However, for other test specimen preparations, the resin was post-cured at 316°C for 16 hours in air. In order to compare properties, the neat resins of the constituent materials, namely Thermid LR-600 and NR-150B2, were also prepared and tested along with the semi-IPN material under identical conditions, except that the NR-150B2 specimen had an  
20 additional curing at 350°C for one-half hour. Table 1 summarizes the physical and mechanical properties of the semi-IPN. The neat resin properties of the constituent materials are given in Table 5.

TABLE 1

Neat Resin Properties of Semi-IPN of  
Therimid LR-600 and NR-150B2

5	Property	
	<sup>a</sup> Glass Transition Temperature, °C	278 and 325
10	<sup>b</sup> Fracture Energy, $G_{1c}$ , J/m <sup>2</sup>	283
	<sup>c</sup> Temperature at 5% wt loss by TGA in Air	465
	<sup>d</sup> Moisture Absorption, %	0.4
15	<sup>a</sup> By TMA; <sup>b</sup> Per ASTM E 399; <sup>c</sup> At a heating rate of 2.5°C/min; <sup>d</sup> two weeks in water at room temperature.	

20

Example 2

Preparation of semi-IPN of Therimid AL-600 and NR-150B2

25 This semi-IPN was prepared by the non-conventional synthetic method which was generally discussed supra.

30 A 59 weight percent resin solution in ethanol was obtained by stirring at room temperature a mixture of 138.6 g of a Therimid AL-600 monomeric precursor solution (75 weight percent solids in ethanol), 42.6 g of an NR-150B2 monomeric precursor solution (61.1 weight percent solids in ethanol) and 38.0 g of anhydrous ethanol. This yielded a viscous dark black solution in which the Therimid AL-600 and NR-150B2 monomeric precursors were present in amounts of approximately 80 and 20 percent, respectively.

To prepare a molding, the solution was concentrated at 100°C for two hours under vacuum (30 in Hg) and then staged at 200°C for one hour in air. Following the cure cycle of Example 1, a neat resin was obtained which had a density of 1.32 g/cc and showed no detectable voids or defects. The physical and mechanical properties of this neat resin listed in Table 2 were determined in Example 1.

TABLE 2

Neat Resin Properties of Semi-IPN of  
Thermid AL-600 and NR-150B2

Property	
<sup>a</sup> Glass Transition Temperature, °C	320
<sup>b</sup> Fracture Energy, $G_{1c}$ , J/m <sup>2</sup>	603
<sup>c</sup> Temperature at 5% wt loss by TGA in Air	490
<sup>d</sup> Moisture Absorption, %	--

<sup>a</sup>By DSC; see Table 1 for footnotes b through d.

25

Example 3Preparation of Semi-IPN of Thermid MC-600 and NR-150B2

This synthesis follows a conventional simultaneous method in which the transimidization reaction described in Example 1 is unlikely to occur, because a fully preimidized prepolymer is used in this synthesis, rather than an amic acid as used in Example 1.

To a solution of 12.3 g of the NR-150B2 solution described in Example 2 was added a mixture of 30.0 g of Thermid MC-600 yellow powder in 60 ml of freshly distilled NMP. Because the Thermid MC-600 powder was not readily soluble in NMP at room temperature, the mixture was warmed and stirred at 50°C for one hour, resulting in a highly viscous gray material. It appeared that there were some insoluble materials present in the solution; and the solution was difficult to stir using a stirring bar, because of its high viscosity. Such a viscous material was concentrated at 176°C for two hours under vacuum (30 in Hg). To reduce its flow and to eliminate the residual solvents, the material was further treated at 200°C for one-half hour under vacuum (30 in Hg). Approximately 14.5 g of the gray molding powder was used to prepare a molding following the cure cycle of Example 1. This afforded a neat resin with a density of 1.37 g/cc. No voids or were seen on the surfaces of this neat resin, the properties of which are shown in Table 3.

TABLE 3

Neat Resin Properties of Semi-IPN of  
Thermid MC-600 and NR-150B2

20

Property	
<sup>a</sup> Glass Transition Temperature, °C	329
<sup>b</sup> Fracture Energy, $G_{1c}$ , J/m <sup>2</sup>	481
<sup>c</sup> Temperature at 5% wt loss by TGA in Air	490
<sup>d</sup> Moisture Absorption, %	--

25

See Table 2 for all footnotes.

30

Example 4Preparation of Semi-IPN of Thermid FA-700 and NR-150B2

5 A 20 weight percent resin solution in NMP was prepared by stirring at room temperature a mixture of 52.0 g of Thermid FA-700 powder, 27.1 g of the NR-150B2 solution described in Example 1, and 264.0 g of freshly distilled NMP. As in Example 3, the resin solution was concentrated to afford a molding powder which was subsequently compression molded. This  
 10 formed a neat resin with a density of 1.32 g/cc. Other properties of this resin are presented in Table 4.

TABLE 4

15 Neat Resin Properties of Semi-IPN of  
 Thermid FA-700 and NR-150B2

Property	
20	<sup>a</sup> Glass Transition Temperature, °C 335
	<sup>b</sup> Fracture Energy, $G_{1c}$ , J/m <sup>2</sup> 306
	<sup>c</sup> Temperature at 5% wt loss by TGA in Air 522
	<sup>d</sup> Moisture Absorption, % --

25 See Table 2 for all footnotes.

TABLE 5

## Neat Resin Properties of Constituent Materials

5	Property	Thermid <sup>®</sup> LR-600 <sup>™</sup> (National Standards)	<sup>®</sup> NR-1502B <sup>™</sup> (DuPont)
	<sup>a</sup> Glass Transition Temperature, °C	290	352
10	<sup>b</sup> Fracture Energy, $G_{1c}$ , J/m <sup>2</sup>	93	2555
	<sup>c</sup> Temperature at 5% wt loss by TGA in Air	460	515
	<sup>d</sup> Moisture Absorption, %	0.3	0.6

See Table 1 for footnotes a through d; e prepared by the present inventor.

15

Example 5Preparation of Celion 6000/Semi-IPN of Thermid LR-600 and NR-150B2

20 For advanced composite applications, the resin solution from Example 1 was used to prepare a prepreg tape by passing a single tow of unsized Celion 6000 graphite fiber through a dip tank and onto a 12-inch diameter multiple speed drum winder wrapped with release paper. This produced a 23.0 cm by 190 cm wet prepreg having a smooth and good tack and drape 25 characteristics. The tape was dried on the rotating drum at room temperature for 16 hours, and then removed from the drum and cut into 7.6 cm by 15.2 cm plies. Twelve plies were tacked unidirectionally and staged at 150°C for one hour. The staged lay-up was placed in a cold matched metal die. This was then inserted into a press preheated to 250°C. A 30 thermocouple was attached to the matched die to determine the temperature. When the die temperature reached 250 C, 500 psi pressure was applied. The composite was cured one hour at 250°C and one hour at 316°C under

500 psi pressure, and then removed from the press when the die temperature reached 177°C. The composite was then postcured at 316°C in air for 16 hours. The ultrasonic C-scan of the composite showed no detectable voids or defects, and thus it was submitted for test specimen  
5 preparations. As a control, a Celion 6000/Therimid LR-600 composite system was also prepared and tested under the identical conditions for the semi-IPN material described above.

The cured control material, however, showed considerable voids detected by the ultrasonic C-scan method. Only the area showing relatively  
10 fewer voids was used for test specimen preparation.

Tables 6 and 11 show the composite properties for the semi-IPN as well as the control material, respectively.

Table 6 compares the physical and mechanical properties of the semi-IPN and its constituent material.

5

TABLE 6

Unidirectional Composite Properties of  
Semi-IPN of Thermid LR-600 and NR-150B2d<sup>d</sup>

10

Property		
	<sup>a</sup> Glass Transition Temperature, °C	312
	Density, g/cm <sup>3</sup>	1.54
15	<sup>b</sup> Flexural Strength, Ksi	
	25°C	254
	232°C	--
	<sup>b</sup> Flexural Modulus, Msi	
	25°C	16.2
20	232°C	--
	<sup>c</sup> Interlaminar Shear Strength, Ksi	
	25°C	7.3
	232°C	--

25

<sup>a</sup>By TMA;

<sup>b</sup>Per ASTM D790;

<sup>c</sup>Per ASTM D2344;

<sup>d</sup>Reinforced with Celion 6000 graphite fibers.

30

Example 6Preparation of Celion 6000/Semi-IPN of Thermid AL-600 and NR-150B2

5 A 59 weight percent resin solution in ethanol from Example 2 was used to prepare a prepreg tape (25.4 cm by 190 cm). The wet prepreg exhibited smooth and good tack and drape characteristics by a visual inspection. It was dried at room temperature for ten hours and then staged at 150°C for one-half hour in air. The staged lay-up was cured as in Example 5. This  
 10 resulted in a high quality composite, as no voids or defects were detected by ultrasonic C-scan. The composite was postcured at 316°C for 16 hours in air and then machined into various specimens for testing.

Table 7 shows the physical and mechanical properties of this composite.

15 TABLE 7  
 Unidirectional Composite Properties of Semi-IPN  
 of Thermid AL-600 and NR-150B2<sup>d</sup>

20	Property	
	<sup>a</sup> Glass Transition Temperature, °C	290 and 330
	Density, g/cm <sup>3</sup>	1.58
	<sup>b</sup> Flexural Strength, Ksi	
	25°C	279
25	232°C	206
	<sup>b</sup> Flexural Modulus, Msi	
	25°C	15.0
	232°C	14.5
	<sup>c</sup> Interlaminar Shear Strength, Ksi	
30	25°C	20.7
	232°C	14.0

See Table 6 for all footnotes.

Example 7Preparation of Celion 6000/Semi-IPN of Thermid MC-600 and NR-150B2

5 As in Example 5, the resin solution (21 percent by weight of solids in  
 NMP) from Example 3 were used to yield a prepreg having an area of 23  
 cm by 190 cm. During the drying process described in Example 5, this  
 prepreg disunited into many pieces. Each piece had a width of about  
 0.6 cm. This made the composite lay-up difficult. Despite this difficulty, a  
 10 high quality composite (7.6 cm by 15.2 cm by 0.2 cm) was obtained following  
 the cure cycle of Example 5.

The physical and mechanical properties for this composite are listed in  
 Table 8.

TABLE 8

15 Unidirectional Composite Properties of  
 Semi-IPN of Thermid MC-600 and NR-150B2d

Property		
20	<sup>a</sup> Glass Transition Temperature, °C	310
	Density, g/cm <sup>3</sup>	1.57
	<sup>b</sup> Flexural Strength, Ksi	
	25°C	293
	232°C	215.5
25	<sup>b</sup> Flexural Modulus, Msi	
	25°C	15.8
	232°C	15.9
	<sup>c</sup> Interlaminar Shear Strength, Ksi	
	25°C	18.5
30	232°C	10.4

See Table 6 for all footnotes.

Example 8Preparation of Celion 6000/Semi-IPN of Thermid FA-700 and NR-150B2

As in Example 5, the resin solution (20 weight percent solids in NMP) from Example 4 was used to impregnate Celion 6000 graphite fibers. The resulting prepreg behaved in a manner similar to that of Example 7. The cured composite was essentially void-free, except that one corner of the composite showed some voids. The composite properties for this system are given in Table 9.

10

TABLE 9  
Unidirectional Composite Properties of  
Semi-IPN of Thermid FA-600 and NR-150B2<sup>d</sup>

15	Property	
	<sup>a</sup> Glass Transition Temperature, °C	315
	Density, g/cm <sup>3</sup>	1.58
	<sup>b</sup> Flexural Strength, Ksi	
20	25°C	264.1
	232°C	185.1
	<sup>b</sup> Flexural Modulus, Msi	
	25°C	14.4
	232°C	14.1
25	<sup>c</sup> Interlaminar Shear Strength,	
	25°C	17.3
	232°C	10.1

See Table 6 for all footnotes.

30

Example 10Preparation of Cross-Ply Composites

To make a realistic assessment of composite microcracking behavior, a  
5 cross-ply composite having a [0,90,0]<sub>s</sub> lay-up was fabricated for the semi-IPN  
of Thermid LR-600 and NR-150B2 and Thermid LR-600 as a control. The  
fabrication of the cross-ply composites follows the same procedure as their  
unidirectional counterparts described in Example 5. Here, AS-4 graphite  
fibers were used, instead of Celion 6000 graphite fibers which were used for  
10 the unidirectional composites. Specimens (1.5 cm by 0.6 cm by 0.13 cm)  
were machined from the cross-ply composites and were subjected to thermal  
cycling. The temperature was varied from -156 to 288°C with a total time  
of 15 minutes for each cycle. Liquid nitrogen was used as a cooling agent.  
After 1000 and 1500 thermal cycles, the unpolished surfaces were examined  
15 by scanning electron microscopy (SEM) at 100 and 2000X magnifications.  
Also, the specimens were immersed in water at room temperature for 1 year  
to determine the amount of water penetrated into the cracks and absorbed  
by the matrix.

TABLE 10  
 Microcracking Behavior of Semi-IPN Cross-Ply Composite Compared  
 with Constituent Material After 1500 Thermal Cycles<sup>a</sup>

Property	Semi-IPN of <sup>b</sup> Therimid LR-600 and NR-150B2	Therimid LR-600 <sup>b</sup>
Type of Microcracks <sup>c</sup>	Mostly Longitudinal	Both Transverse and Longitudinal Microcracks
Type of Microcrack Failure <sup>d</sup>	At the Interface Between Fiber and Matrix as well as in the Matrix	Only at the Fiber-Matrix Interface
Moisture Absorption, %		
As Fabricated	1.3	1.8
After 1500 Thermal Cycles	1.8	3.3

<sup>a</sup>Temperature varied from -156 to 288°C; <sup>b</sup>Reinforced with AS-4 graphite fibers and had [0,90,0]<sub>s</sub> layup; <sup>c</sup>By SEM at 100X magnification; <sup>d</sup>By SEM at 2000X magnification; <sup>e</sup>One year in water at 25°C.

TABLE 11  
Unidirectional Composite Properties of Constituent Materials

	Property	Thermid AL-600 <sup>a</sup>	Thermid MC-600 <sup>b</sup>	Thermid IP-600 <sup>c</sup>
5	Glass Transition Temperature, °C <sup>a</sup>	--	--	--
	Density, g/cc	1.50	--	--
	Flexural Strength, Ksi			
10	25°C	--	195.0	130.0
	316°C	--	148.0	78.0 <sup>d</sup>
	Flexural Modulus, Msi			
	25°C	--	15.0	--
	316°C	--	12.0	--
15	Interlaminar Shear Strength, Ksi			
	25°C	9.6	12.1	7.3
	316°C	4.5	8.0	5.0 <sup>d</sup>

<sup>a</sup>Prepared and tested by the present invention using the same cure cycle as  
20 the Semi-IPN materials; <sup>b</sup>Reported by National Starch and Chemical  
Corporation, reinforced with Hercules HTS fibers and postcured four hours  
at 343°C and four hours at 371°C; <sup>c</sup>Reported by A. L. Landis and A.B.  
Naselow NASA CP 2385 (1983); <sup>d</sup>Tested at 288°C.

25

What is claimed as new and desired to be secured by Letters Patent of  
the United States is:

~~Not for Dissemination - These  
claims are in the pending  
application and may not be  
allowed.~~

LAR 14339-1

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PATENT APPLICATION

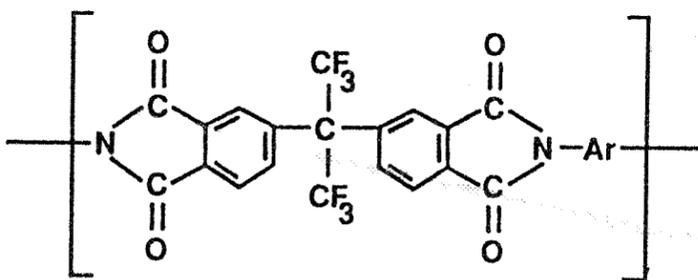
A TOUGH HIGH PERFORMANCE SIMULTANEOUS  
SEMI-INTERPENETRATING POLYMER NETWORK

Abstract of the Disclosure

5

A semi-interpenetrating polyimide network and methods for making and using the same are disclosed. The semi-IPN system comprises a high performance thermosetting polyimide having an acetylene-terminated group acting as a crosslinking site and a high performance linear thermoplastic polyimide having the following repeating unit:

10

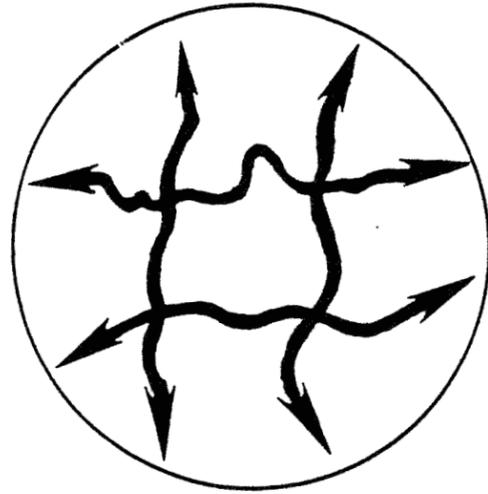


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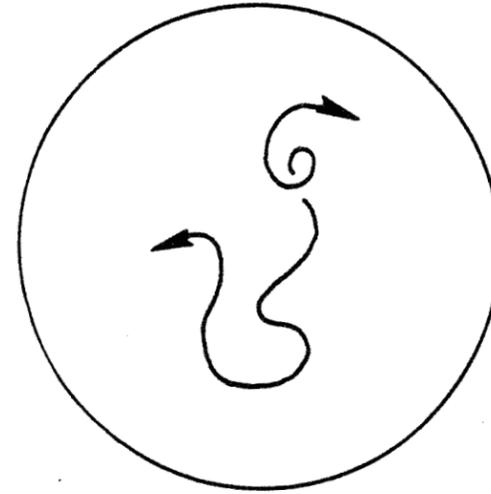
The polymer is made by combining low viscosity precursors and low molecular weight polymers of the thermosetting and thermoplastic polyimides and allowing them to react in the immediate presence of each other to form a simultaneous semi-interpenetrating polyimide network. Provided is a high temperature system having significantly improved processability and damage tolerance while maintaining excellent thermo-oxidative stability, mechanical properties and resistance to humidity, when compared with the commercial high temperature resin, Thermid 600. This material is particularly adapted for use as a molding, adhesive and advanced composite matrix for aerospace structural and electronic applications.

25

# CONCEPT OF SEMI-INTERPENETRATING POLYIMIDE NETWORK SYNTHESIS



+

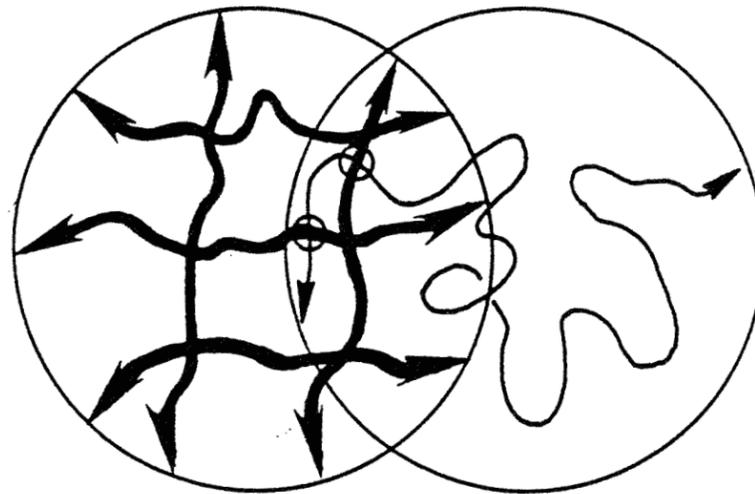


Addition type thermosetting polyimide

- Easy to process
- Brittle

Condensation type thermoplastic polyimide

- Difficult to process
- Tough



Semi-IPN

- Easy to process
- Tough

NASA Case No. LAR 14339-1  
RUTH H. PATER ET AL  
SHEET 1 OF 1