

P-21

NASA CASE NO. LAR 15229-¹2-CU

PRINT FIG. N/A

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Serial No.: 08/186,054
01/18/94

LaRC

(NASA-Case-LAR-15229-1-CU)
POLY(ARYLENE ETHER-CO-IMIDAZOLE)S
AS TOUGHNESS MODIFIERS FOR EPOXY
RESINS Patent Application (NASA.
Langley Research Center) 21 p

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AWARDS ABSTRACT

POLY(ARYLENE ETHER-CO-IMIDAZOLE)S AS TOUGHNESS MODIFIERS FOR EPOXY RESINS

NASA Case No. LAR 15229-1-CU

Thermosetting materials based on epoxy chemistry were one of the first systems developed for use as coatings, adhesives and composite matrices. The use of high temperature thermosetting materials in composites is a major area of interest. Fiber-reinforced organic composites for aerospace structural applications offer the advantages of higher strength to weight ratios, improved fatigue characteristics, corrosion resistance and higher stiffness (modulus) as compared to their metal counterparts. Epoxies offer certain advantages over other materials such as low density, tack, drape, processability, and low cost. Once cured, these polymers exhibit high glass transition temperatures (T_g) and good mechanical properties.

By the present invention, poly(arylene ether-co-imidazole)s (PAEI) were prepared by reacting an aromatic bisphenol, a bisphenol imidazole and an activated aromatic dihalide or dinitro compound in the presence of potassium carbonate in a polar aprotic solvent at elevated temperatures under nitrogen. The resulting PAEI is a random copolymer having pendant imidazole units along the polymer backbone. These imidazole units provide reactive sites for an epoxy. The distance between PAEI-epoxy crosslinks can be controlled by varying the amount of imidazole present along the polymer backbone. The distance between the epoxy end groups and the PAEI units is less than that obtained with thermoplastic oligomers in which reactive sites are only at the ends. A comparison of the PAEI modified epoxies with those of the prior art shows that the PAEI modified system had a significantly greater increase in the fracture toughness.

The novelty of this invention resides in the structure of the poly(arylene ether-co-imidazole). By controlling the molecular weight, these polymers are soluble in epoxy at high concentrations. As a result, the modified system is tough with only a limited decrease in the glass transition temperature.

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POLY(ARYLENE ETHER-CO-IMIDAZOLE)S AS TOUGHNESS MODIFIERS
FOR EPOXY RESINS

Origin of the Invention

5 The invention described herein was jointly made by employees of the United States Government and a contract employee in the performance of work under NASA Grant number NCC1-150 and is subject to the provisions of Public Law 96-517 (35 U.S.C. 202) in which the contractor has elected not to retain title.

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Background of the Invention

1. Field of the Invention

 The present invention relates to epoxies. In particular, it relates to the toughening of epoxies using poly(arylene ether-co-imidazole)s as modifiers.

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2. Description of the Related Art

 Thermosetting materials based on epoxy chemistry were one of the first systems developed for use as coatings, adhesives and composite matrices. The use of high temperature thermosetting materials in composites is a major area of interest. Fiber-reinforced organic composites for aerospace structural applications offer the advantages of higher strength to weight ratios, improved fatigue characteristics, corrosion resistance and higher stiffness (modulus) as compared to their metal counterparts. Epoxies offer certain advantages over other materials such as low density, tack, drape, processability, and low cost. Once cured, these polymers exhibit high glass transition temperatures (T_g) and good mechanical properties.

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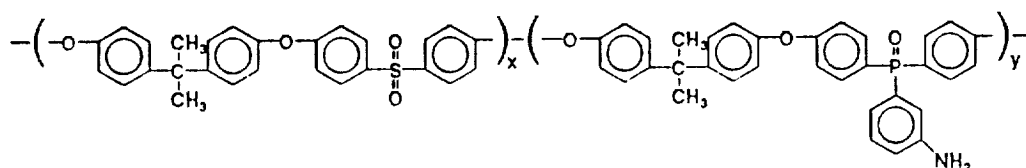
 Despite these advantages, epoxies have several deficiencies which restrict their use in certain applications. A fully cured epoxy resin is comprised of a highly crosslinked complex matrix which causes the cured polymer to be brittle or lack damage tolerance. In addition, epoxies have high moisture

absorption and limited thermo-oxidative stability.

In order to use epoxies as structural materials for the aerospace industry, the polymer must exhibit rigidity, resistance to creep, high T_g and high impact strength or damage tolerance. However, damage tolerance and/or high impact strength are qualities of elastomers rather than thermosets. This is currently the major problem in designing commercially viable high performance resins.

To overcome this deficiency, several approaches have been taken which provide a toughened epoxy system whose morphology allows for toughness and stability while under stress at elevated temperatures without having an adverse affect on the modulus, T_g and processability of the polymer. The most widely used method of thermoset modification has been by the dispersion of a ductile second phase into the matrix. Predispersion of rubber particles into an epoxy resin, prior to curing, generally improves fracture toughness but compromises thermal resistance and hot/wet properties. The development of a low cost epoxy with improved toughness while maintaining its other properties would greatly expand the use and broaden the market for these materials.

Blends of thermosets with elastomers, glassy thermoplastics or reactive thermoplastics are being evaluated as potential toughening matrices wherein specific attributes of several polymers are combined in a single material. An example of a reactive thermoplastic modified epoxy is described in Pak et al. ("Synthesis and Characterization of Novel Toughened Thermosets Derived from Pendent Amines on the Backbone of Poly(arylene ether sulfone)s", Polymer, Volume 34, Number 4, 1993.). They randomly incorporated pendent aryl amines onto the backbone of poly(arylene ether sulfone)s to give copolymers which have the following structure:



and subsequently reacted them with liquid epoxy resin and 4,4'-diamino-diphenylsulfone (DDS). It was demonstrated that selected compositions could significantly improve the fracture toughness of the epoxy networks. For a poly(arylene ether sulfone) having a 2.5 mole percent crosslink site which was loaded at 25 weight percent into epoxy, the fracture toughness was 2.28 ± 0.43 MNm^{-3/2} as compared to the control which had a fracture toughness of 0.75 ± 0.08 MNm^{-3/2}. However, at a 10 weight percent loading of the same polymer into the epoxy, the fracture toughness was only 0.92 ± 0.06 MNm^{-3/2}. It was also observed that when the concentrations of the crosslink site of the reactive thermoplastic toughener increased, there was relatively little improvement in the fracture toughness.

In another case where reactive thermoplastics are used as toughening agents, thermoplastic oligomers endcapped with a reactive group (i.e. phenol, amine, or epoxy) are blended into the epoxy. The system is cured and the thermoplastic is incorporated into the matrix via the reactive end group. Hedrick et al. ("Chemical Modification of Matrix Resin Networks with Engineering Thermoplastics: 1. Synthesis, Morphology, Physical Behavior and Toughening Mechanisms of Poly(arylene ether sulfone) Modified Epoxy Networks", Polymer, Volume 32, number 11, 1991.) modified epoxy resins with either phenolic hydroxyl or aromatic amine terminated aryl ether sulfone oligomers and thermally cured them with 4,4'-diaminodiphenyl sulfone. The aryl ether sulfone oligomers were miscible with the epoxy precursor and upon network formation a two phase structure developed in which the polysulfone formed discrete particles evenly dispersed in the epoxy matrix. The resulting networks showed an increase in fracture toughness from 0.6×10^6 MNm^{-3/2} (control) to 0.8×10^6 MNm^{-3/2} (for 10%) to 1.1×10^6 MNm^{-3/2} (for 15%).

An object of the present invention is to increase the toughness of epoxies by reacting the epoxy with poly(arylene ether-co-imidazole)s.

Another object of the present invention is to prepare molded parts from the toughened epoxies.

Another object of the present invention is to prepare composites from the toughened epoxies.

Summary of the Invention

5 Poly(arylene ether-co-imidazole)s (PAEI) were prepared by reacting an aromatic bisphenol, a bisphenol imidazole and an activated aromatic dihalide or dinitro compound in the presence of potassium carbonate in a polar aprotic solvent at elevated temperatures under nitrogen. The resulting PAEI is a random copolymer having pendant imidazole units along the polymer backbone.

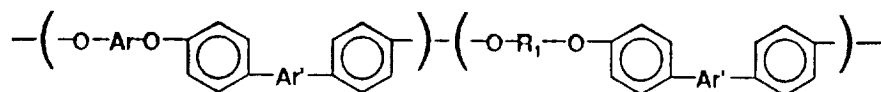
10 These imidazole units provide reactive sites for an epoxy. The distance between PAEI-epoxy crosslinks can be controlled by varying the amount of imidazole present along the polymer backbone. The distance between the epoxy end groups and the PAEI units is less than that obtained with thermoplastic oligomers in which reactive sites are only at the ends. A

15 comparison of the PAEI modified epoxies with the poly(arylene ether sulfone) modified epoxies of Pak et al. shows that the PAEI modified system having a 10 mole percent crosslink site and a 10 weight percent reactive thermoplastic exhibited an increase in fracture toughness of 1.75 fold. This is significantly greater than the fracture toughness reported by Pak et al. for their epoxies

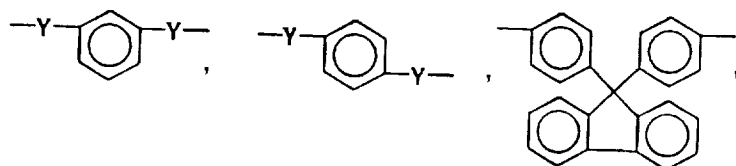
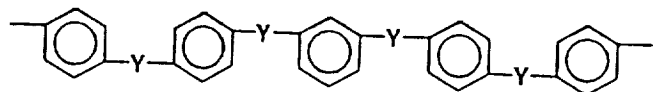
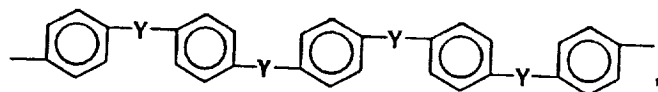
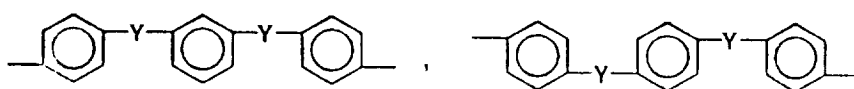
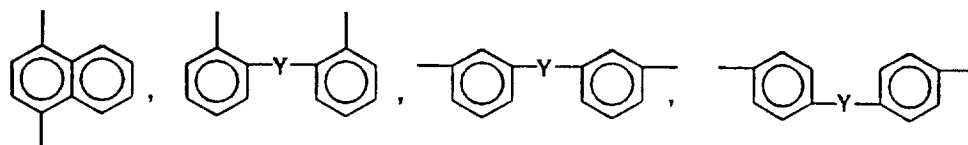
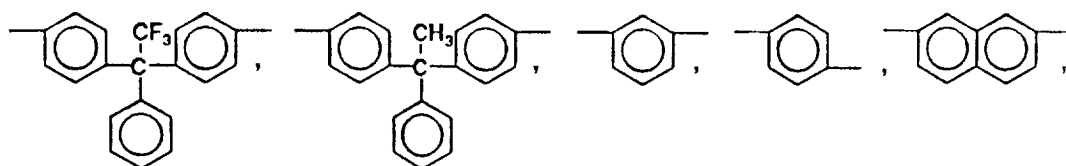
20 which were modified with poly(arylene ether sulfone)polymer having the same percentage of crosslink sites and reactive thermoplastic. For this system, Pak et al. reported an increase in fracture toughness from $0.75 \pm 0.08 \text{ MNm}^{-3/2}$ (control) to $0.84 \pm 0.12 \text{ MNm}^{-3/2}$.

Description of the Preferred Embodiments

25 The poly(arylene ether co-imidazole)s of the present invention have the repeat unit:



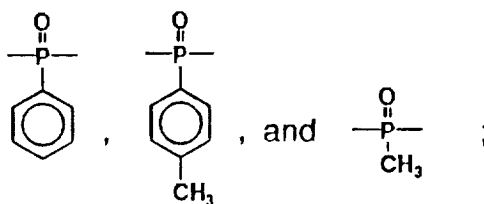
wherein Ar is a member selected from the group consisting of:



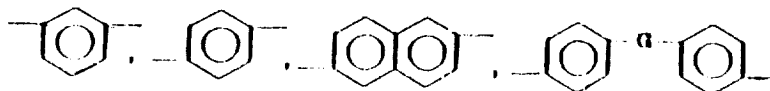
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25 wherein Y is a member selected from the group consisting of: a direct bond, -O-, -S-, -CO-, -SO₂-, -CH₂-, -C(CH₃)₂-, -C(CF₃)₂-,

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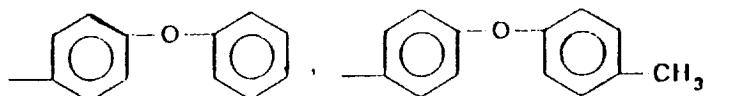
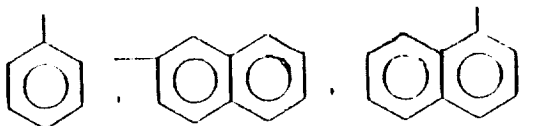
wherein R_2 is a member selected from the group consisting of:



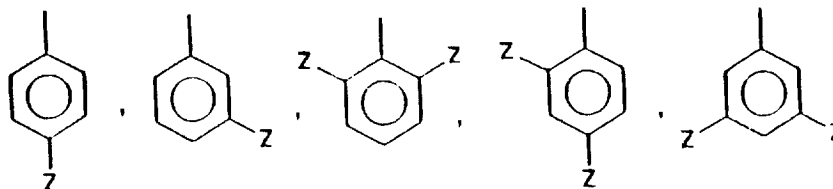
5 wherein G is a member selected from the group consisting of: a direct bond, $-CH_2-$, $-O-$, $-S-$, $-CO-$, and $-SO_2-$;

wherein R_3 is a member selected from the group consisting of: $-H$, $-CH_3$, $-CH_2CH_3$, $-OCH_3$, $-CF_3$,

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wherein Z is a member selected from the group consisting of: $-CH_3$, $-CF_3$, $-OCH_3$, $-NO_2$, $-I$, $-Cl$, $-Br$, $-F$, $-CH_2CH_3$, and phenyl; and

wherein the ratio of

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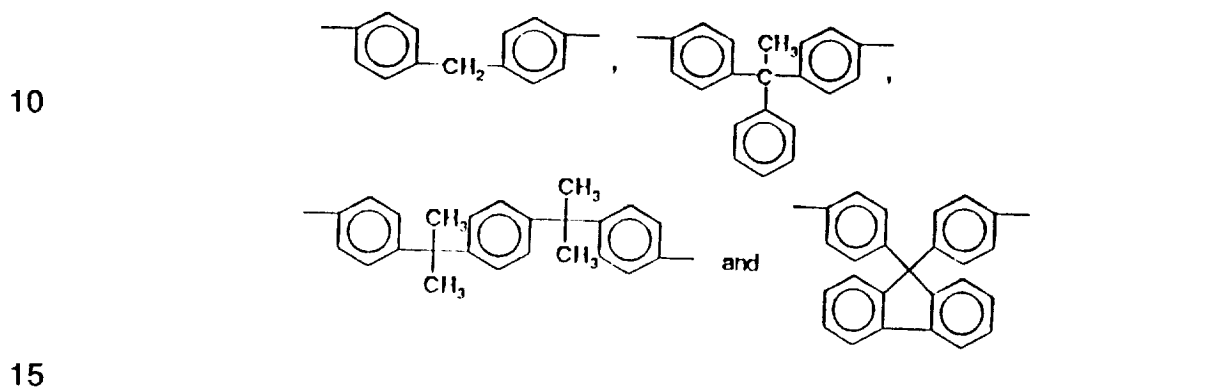
ranges from about 99 to 1 to about 1 to 99.

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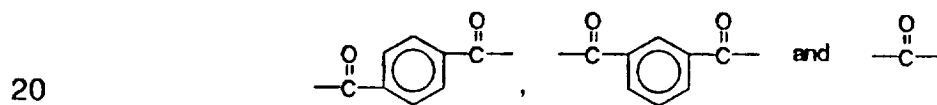
In a preferred embodiment of the invention, this ratio is 90 to 10.

Of particular mention is that when a phosphine oxide unit is selected for an Ar' and/or a Y substituent, not only does the copolymer offer increased toughness to the epoxy but it also causes the final composition to be atomic oxygen resistant. This is important for low earth orbit space applications where atomic oxygen resistance is necessary.

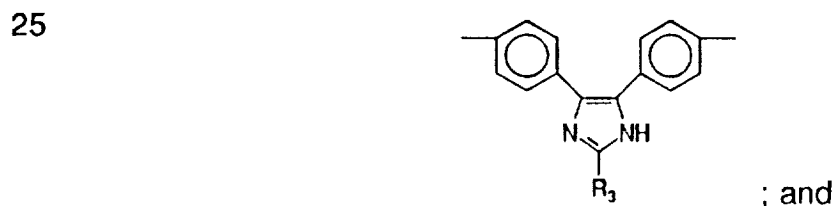
In a preferred embodiment of the invention, Ar is a member selected from the group consisting of:



Ar' is a member selected from the group consisting of:



R₁ is

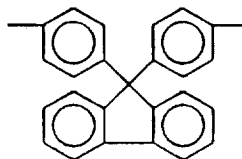


R₃ is phenyl.

The modified epoxies prepared with these particular PAEIs showed a significant increase in toughness with only a 10 weight percent loading of the PAEI.

In a most preferred embodiment, Ar is

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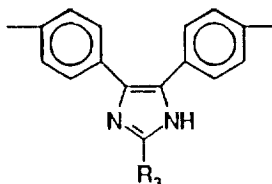


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;

Ar' is -CO-; R₁ is

15



; and

R₃ is phenyl.

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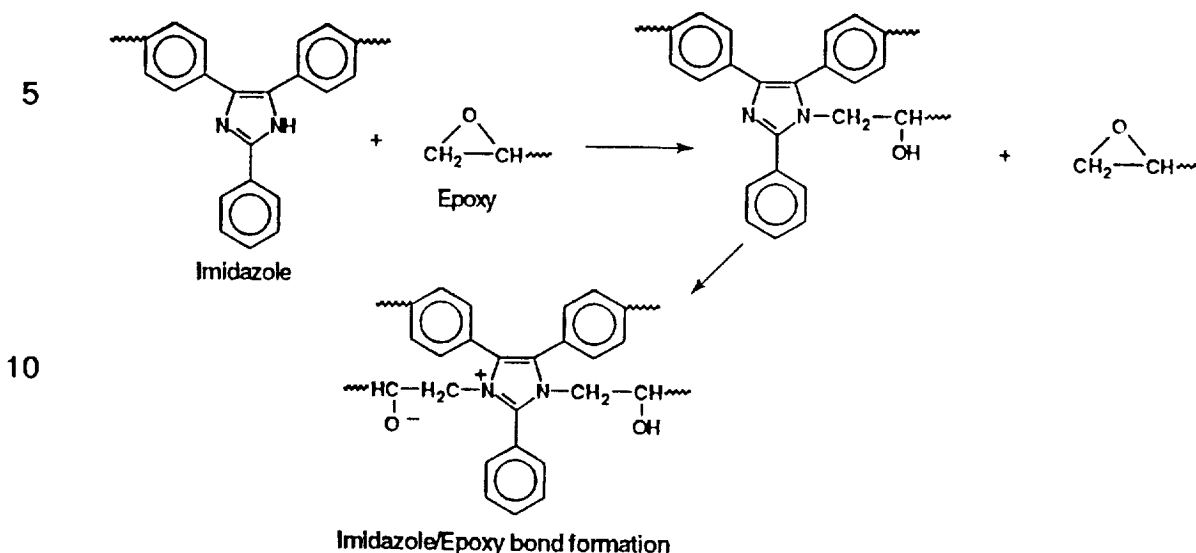
This particular PAEI exhibited the highest degree of solubility in the epoxy resin while maintaining a favorable T_g. In addition, it gave significantly improved toughness results as compared to samples prepared using other PAEIs to toughen the epoxies.

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In preparing the toughened epoxy, the epoxy resin which was preferred for the present invention was that of N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzenamine which is commercially available from Ciba-Geigy Corporation as Araldite® XU MY 722. The PAEI was added to the epoxy resin and allowed to react at 100°C until a homogeneous melt was obtained. A stoichiometric ratio of epoxide equivalent weight to the preferred curing agent, 4-aminophenyl sulfone, commercially available from Aldrich Chemical Company

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as 4,4'-DDS, was added to the mixture. A vacuum was applied throughout the process to degas the system. The following scheme shows the reaction mechanism for the reaction of a PAEI with an epoxy.



Test specimens were hot-melt cast into RTV silicone molds and cured according to the following cure cycle: 1 hour at 80°C; 1 hour at 100°C; 4 hours at 150°C; and 6 hours at 200°C. The specimens were slowly cooled to room temperature prior to removal from the molds. This same cure cycle is followed for preparing composites.

The T_g, solution viscosity and solubility in the neat epoxy resin were measured for a series of PAEIs having various molecular weights. Inherent viscosities ranged from 0.42 to 0.91 dL/g for the PAEIs. The T_gs for these PAEIs ranged from 147° to 237°C. All of the soluble systems formed tough, creasable films.

Polymer solubility in the neat epoxy resin facilitated processing of the modified resins. A polymer T_g close to that of the cured epoxy system was targeted to maintain use temperature.

High molecular weight PAEIs were found to have a limited solubility in the epoxy resin making incorporation of high thermoplastic loadings difficult. Therefore, a controlled molecular weight version was prepared using bis(4-fluorophenyl)ketone, 9,9-bis(4-hydroxyphenyl)fluorene (90%) and 2-phenyl-4,5-

bis(4-hydroxyphenyl)imidazole (10%). This controlled molecular weight PAEI was found to be soluble in the epoxy at high concentrations which results in toughened modified systems with a limited decrease in glass transition temperatures.

5 Neat resin moldings for the high molecular weight polymer were fabricated at 340°C for 1 hour at 300 psi. The moldings were well consolidated and void free. Miniature compact tension specimens yielded stress intensity factors of $1.83 \text{ MNm}^{-3/2}$ when tested at room temperature. The modified epoxy specimens were opaque with slightly crazed fracture surfaces indicative of
10 ductile failure while unmodified epoxy specimens had clear, smooth fracture surfaces which is indicative of brittle fracture. The stress intensity factors for the notched three point bend fracture specimens exhibited increased toughness with increasing polymer content.

 The modified system undergoes a phase separation during cure as
15 indicated by increasing turbidity with increasing polymer concentration and was confirmed by Scanning Electron Microscopy. This phase separation is desirable because separation during cure of a predominately thermoplastic second phase serves as an energy absorbing mechanism enhancing crack resistance and toughness.

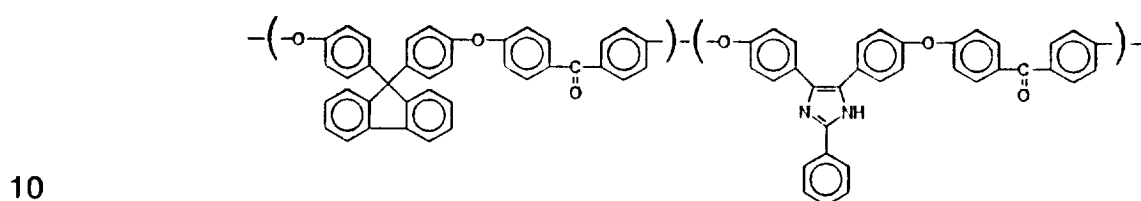
20 The following are examples which illustrate the preparation and use of PAEIs in epoxy systems for applications such as composites and molded parts. These examples are merely illustrative and intended to enable those skilled in the art to practice the invention in all of the embodiments flowing therefrom, and do not in any way limit the scope of the invention as defined by the claims.

25

EXAMPLES

Example 1

5 The following example illustrates the reaction sequence for the synthesis of a poly(arylene ether-co-imidazole) having the following repeat unit:



15 Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed 9,9-bis(4-hydroxyphenyl)fluorene (80.8804 g, 0.23 mol), 2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole (8.4213 g, 0.03 mol), bis(4-fluorophenyl)ketone (55.9597 g, 0.26 mol), pulverized anhydrous potassium carbonate (81.52 g, 0.59 mol, 15% excess), dry N,N-dimethylacetamide (DMAc) (540 ml, 20% solids) and toluene (80 ml). The mixture was heated to about 135°C for four

20 hours and then heated to 155°C overnight under nitrogen. The viscous yellow solution was precipitated into a water/acetic acid mixture, collected, washed successively in water and methanol and dried at 125°C. The yield was 97.8 g (72%) of white polymer having a glass transition temperature of 237°C. The inherent viscosity of a 0.5% solution in chloroform at 25°C was 0.63 dL/g.

25 The same procedure was followed to prepare poly(arylene ether-co-imidazole)s which had the same repeat unit but differed by the stoichiometric ratio of 9,9-bis(4-hydroxyphenyl)fluorene to bis(4-fluorophenyl)ketone where the amount of 2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole remained constant at 10 mole percent of the copolymer. The copolymer stoichiometry is summarized

30 in Table 1 and the final neat copolymer properties are summarized in Table 2.

Table 1

1:1 Stoichiometry	Polymer 1
10 mole % offset favoring bisphenol	Polymer 2
10 mole % offset favoring dihalide	Polymer 3
5 mole % offset favoring bisphenol	Polymer 4
5 mole % offset favoring dihalide	Polymer 5

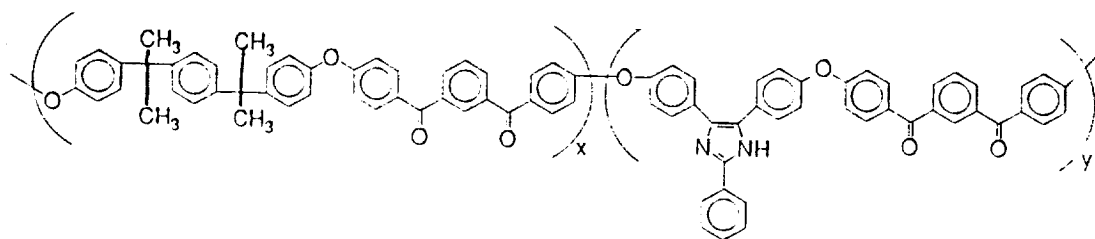
Table 2

Polymer	M_n^a (g/mol)	TGA ^b (°C)	$[\eta]^c$ dL/g	η_{inh}^d dL/g	Tg ^e (°C)
1	4814	458.1	0.498	0.34	243
2	3505	430.5	0.183	0.16	223
3	2524	461.0	0.143	0.13	205
4	5478	430.5	0.279	0.23	251
5	4294	491.5	0.222	0.19	226

^aGel Permeation Chromatography/Differential Viscometry^bTGA at 2.5°C/min^cInherent Viscosity in unstabilized tetrahydrofuran at 35°C with
0.5% wt% solutions^dIntrinsic Viscosity in N-methylpyrrolidone with 0.02 molar LiBr at 60°C^eDifferential Scanning Calorimetry 20°C/min

Example 2

Another poly(arylene ether-co-imidazole) was prepared which has the following structure:



15

Into a 100 ml three neck round bottom flask equipped with a mechanical stirrer, thermometer, nitrogen inlet, moisture trap and reflux condenser was placed [(4-hydroxyphenyl)-2-propyl]benzene (12.4339 g, 35.89 mmol), 2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole (1.3094 g, 3.99 mmol), 1,3-bis(4-fluorobenzoyl)benzene (12.8522 g, 39.87 mmol), pulverized anhydrous potassium carbonate (19.01 g, 137.54 mmol, 15% excess), dry N,N-dimethylacetamide (DMAc) (107 ml, 20% solids) and toluene (45 ml). The mixture was heated to about 135°C for four hours and then heated to 155°C overnight under nitrogen. The viscous orange solution was precipitated into a

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water/acetic acid mixture, collected, washed successively in water and methanol and dried at 125°C. The yield was 22.14 g (89%) of white polymer having a glass transition temperature of 158°C. The inherent viscosity of a 0.5% solution in DMAc at 25°C was 0.48 dL/g.

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The same procedure was followed to prepare poly(arylene ether-co-imidazole)s which had the same chemical composition but differed by the ratio of [(4-hydroxyphenyl)-2-propyl]benzene to 2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole with the molar amount of 1,3-bis(4-fluorobenzoyl)benzene remaining constant at a stoichiometric ratio of 1:1. Table 3 summarizes the various properties for the polymers prepared with varying [(4-hydroxyphenyl)-2-propyl]benzene/2-phenyl-4,5-bis(4-hydroxyphenyl) imidazole ratios.

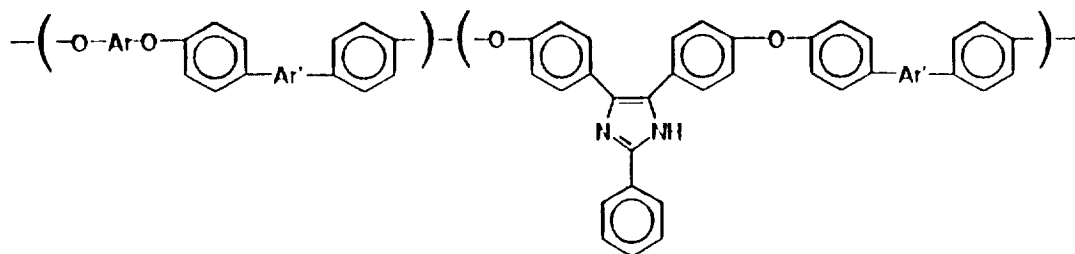
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Table 3.

X:Y	T _g (°C)	Temp. of 5% Weight Loss [†] (°C)	Intrinsic Viscosity ^g (dL/g)
100:0	157	402	0.70
90:10	159	404	0.44
70:30	171	367	0.44
50:50	185	425	0.42
30:70	199	387	0.42
90:10	213	367	--
0:100	220	374	0.55

[†] TGA at 2.5°C/min^g 35°C in THFExample 3

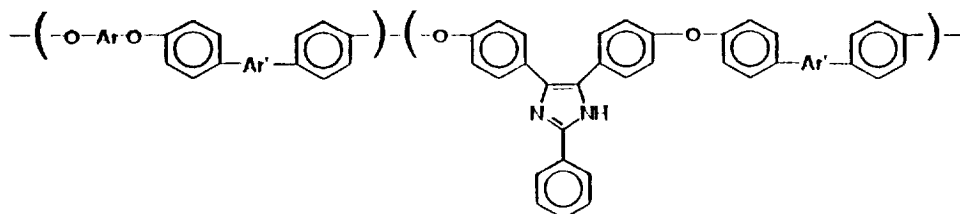
The procedures for Examples 1 and 2 were followed to prepare other poly(arylene ether-co-imidazole)s which have the repeat unit:



where the backbone of the copolymer was varied and the mole percent of the

imidazole crosslink site remained at 10 mole percent. The T_g and inherent viscosities for these copolymers are given in Table 4.

Table 4



Ar	Ar'	Mole % Imidazole	T_g , °C	η_{inh} , dL/g (solvent)
		10	147	-----
		10	186	0.91 (THF)
		10	207	0.50 (CH ₂ Cl ₂)
		10	171	0.48 (DMAc)
		10	237	0.63 (CHCl ₃)

Example 4

Into 125 ml reaction vessel equipped with a mechanical stirrer and vacuum evacuation outlet, was placed 40.14 g (62% w/w) N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzenamine, 6.5 g (10 % w/w) of the polymer represented in example 1. The mixture was stirred at 100°C until a clear homogeneous melt was obtained. 18.29 g (28% w/w) of 4,4'-diaminodiphenylsulfone (DDS) were charged into the vessel, the mixture was stirred and heated at 100°C until the DDS dissolved. The resin was degassed under vacuum for 20 min. The glass transition temperatures obtained by DSC at 20°C/min for the modified epoxy resin system are summarized in Table 5.

Table 5

Weight % Polymer	Tg (°C)
0	190
5	186
10	151
20	154, 224

Example 5

The resin prepared in Example 4 was hot-melt cast into RTV silicone molds and cured according to the following cycle: 1 hour at 80°C; 1 hour at 100°C; 4 hours at 150°C; and 6 hours at 200°C. The specimens were slowly cooled to room temperature prior to removal from the molds and tested in accordance with ASTM E-399. Notched three point bend specimens yielded

an increase in fracture toughness of 1.7 fold for the modified epoxy resin.

Table 6 compares the test data to that of the related art.

Table 6

Weight % Polymer	K_{Ic} MN/m ^{3/2}	K_{Ic}^h MN/m ^{3/2}	K_{Ic}^i MN/m ^{3/2}
0(control)	0.388 ±0.02	0.75±0.08	0.6
5	0.528 ±0.03	0.75±0.06	--
10	0.660 ±0.05	0.84±0.12	0.8
15	--	0.85±0.04	1.1
20	--	0.89±0.06	--

^h Pak et al. 1993

ⁱ Hedrick et al. 1991

Example 6

A prepreg for a composite part is prepared by coating carbon fibers with the modified epoxy resin prepared in Example 4. The prepreg material is then stacked in a mold and cured according to the following cycle: 1 hour at 80°C; 1 hour at 100°C; 4 hours at 150°C; and 6 hours at 200°C. The composite specimen is slowly cooled to room temperature prior to removal from the mold.

POLY(ARYLENE ETHER-CO-IMIDAZOLE)S AS TOUGHNESS MODIFIERS
FOR EPOXY RESINSAbstract of the Disclosure

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A toughened epoxy was prepared by reacting an epoxy resin with a poly(arylene ether-co-imidazole) (PAEI). The epoxy resin comprises N,N,N',N'-tetraglycidyl-4,4'-methylenebisbenzenamine and 4-aminophenyl sulfone. The PAEI was prepared by reacting an aromatic bisphenol, a bisphenol imidazole and an activated aromatic dihalide or dinitro compound in the presence of potassium carbonate in a polar aprotic solvent at an elevated temperature. The epoxies which were modified with these particular PAEIs showed a significant increase in toughness with only a 10 weight percent loading of the PAEI into the epoxy. These toughened epoxies were used to prepare composites and molded parts.

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