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(54) Title: BLENDS OF COPOLY(ARYLENE SULFIDE) AND POLY(ARYL SULFONE)

(57) Abstract

Disclosed is a composition comprising an admixture of (A) from 99 to 1 weight percent, based on the weight of the admixture, of a copoly(arylene sulfide) and (B) from 1 to 99 weight percent, based on the weight of the admixture, of a poly(aryl sulfone).

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BLENDS OF COPOLY(ARYLENE SULFIDE) AND POLY(ARYL SULFONE)

This invention relates to blends of a copoly(arylene sulfide) and a poly(aryl sulfone).

Poly(arylene sulfide) resins are thermoplastic polymeric materials with good thermal stability, unusual insolubility, resistance to chemical environments and inherent flame resistance. Poly(arylene sulfide) resins additionally have good electrical insulative properties which make them ideal for electrical and electronic applications. Their excellent resistance to chemical degradation makes them ideal for use in chemical environments which involve organic solvents and strong mineral acids, such as coatings for pipes, tanks, pumps and other equipment. These polymers can be prepared by reacting p-dichloro-benzene with sodium sulfide in a polar organic solvent to produce poly(phenylene sulfide) and the by-product sodium chloride in accordance with U.S. 2,513,188 and U.S. 2,538,941. An improvement on this procedure involves adding N-haloamides as catalysts.

Recently copoly(arylene sulfides) have been discovered. These polymers can be described as having repeating units corresponding to the structure

$$[\ (-A-S)_{1-x}(-A-S-S-)_x]_n$$

wherein x is in the range of 0.5 to 0.001, A is a divalent aromatic radical and n is at least 200 and is preferably in the range of 500 to 5,000.

It has now been discovered that copoly(arylene sulfide) can be blended with poly(aryl sulfone). This blend can be broadly described as an admixture of

(A) from 99 to 1 weight percent, based on the weight of the admixture, of a copoly(arylene sulfide) corresponding to the structure

$$[\ (-A-S)_{1-x}(-A-S-S-)_x]_n$$

wherein A is a divalent substituted or unsubstituted aromatic radical, x is in the range of 0.5 to 0.001 and n is at least 25, and

(B) from 1 to 99 weight percent, based on the weight of the admixture, of a poly(arylsulfone).

Blends of poly(phenylene sulfide) and poly(aryl sulfone) are disclosed in U.S. 4,021,596.

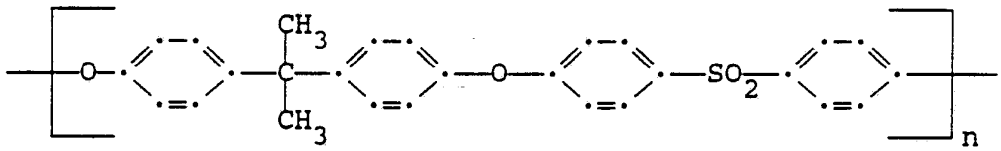
The copoly(arylene sulfide) polymers useful in this invention are identical to the copoly(arylene sulfide) polymers disclosed in U.S. 4,786,713 and U.S. 4,855,393, herein incorporated by reference, except that the minimum value of n of the copoly(arylene sulfide) polymers useful in this invention is lower than the minimum value of n for the copoly(arylene sulfide) polymers which is disclosed in these references. The copoly(arylene sulfide) polymers useful in this invention are therefore inherent in the disclosure of these references because as the molecular weight builds up toward the minimum value of n of at least 200 which is disclosed in these references the molecular weight passes through a molecular weight associated with the lower minimum value of n of 25 of the copoly(arylene sulfide) polymers of this invention. The copoly(arylene sulfide) polymers useful in this invention can be prepared by those skilled in the art by following the teachings of these references and controlling the stoichiometry, time, temperature and other variables of

the reaction to achieve a molecular weight associated with a value of n which is at least 25.

The diiodoaromatic compounds which can be utilized to prepare the copoly(arylene sulfide) useful in this invention, include unsubstituted or substituted aromatics which have two iodine substituents. Preferred diiodoaromatic compounds are the diiodobenzenes, diiodonaphthalenes and diiodobiphenyls which may be unsubstituted or substituted. More preferably the diiodoaromatic compounds suitable for the present invention include p—diiodobenzene, m—diiodobenzene, p,p'—diiodobiphenyl, p,p'—diiodobiphenyl, p,p'—diiododiphenyl ether and 2,6—diiodonaphthalene. Most preferably the diiodo compound is p—diiodobenzene.

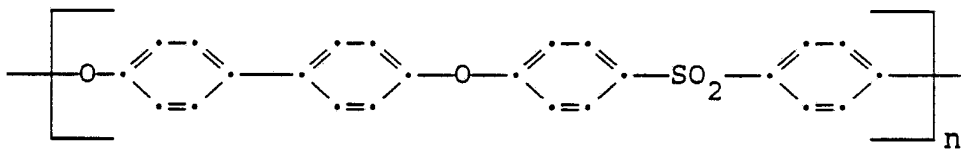
The poly(aryl sulfone) polymers useful in this invention and the method of their preparation are well known in the art and are described in U.S. 4,021,596 and European Patent Application 0 170 065.

In one preferred embodiment of this invention the poly(aryl sulfone) corresponds to the structure



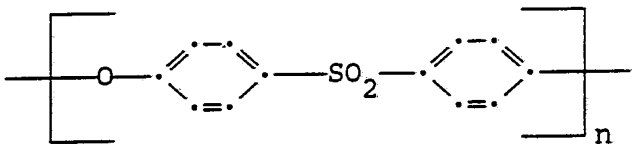
where n is at least 15.

In another preferred embodiment of this invention the poly(aryl sulfone) corresponds to the structure



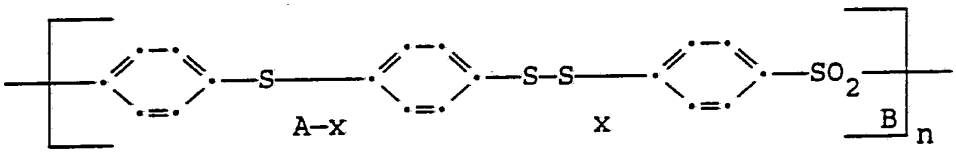
where n is at least 15.

In still another preferred embodiment of this invention the poly(aryl sulfone) corresponds to the structure



where n is at least 25.

In an optional embodiment of this invention the composition can further contain from 0.1 to 25 weight percent, based on the combined weight of the copoly(arylene sulfide) and poly(aryl sulfone), of a poly(cophenylene sulfide phenylene sulfone) corresponding to the structure



wherein A is in the range of 0.95 to 0.05, B is in the range of 0.05 to 0.95 and x is in the range of 0.001 to 0.5 and n is at least 25.

The poly(cophenylene sulfide phenylene sulfone) is known in the art and can be prepared in accordance the disclosure of U.S. 4,786,713 using a diiodo sulfone as a starting material.

The blends of this invention can be prepared by known techniques for blending polymers. For example, the polymers can be coextruded in convention twin screw extrusion equipment. Also, powders of both polymers may be admixed and the admixed powders extruded in a single screw extruder. Preferably, an admixture of powdered polymer is prepared and the admixture powder is extruded in a single screw extruder.

The amount of copoly(arylene sulfide) is in the range of 99 to 1 weight percent, preferably 85 to 15 weight percent, based on the weight of the admixture. The amount of poly(aryl sulfone) is in the range of 1 to 99 weight percent, preferably 15 to 85 weight percent, based on the weight of the admixture.

The compositions of this invention can be used for preparation of various shaped articles such as pellets, fibers and molded articles. The polymer can be prepared into these shaped articles by conventional processes, such as injection molding, melt spinning, and melt extrusion.

The compositions of this invention can additionally contain fillers, nucleating agents and reinforcing materials in the form of fibers, minerals, powders or mats. For example, the compositions can contain glass fibers, aluminum oxide, calcium oxide, silicon dioxide, Titanium dioxide, copper, kaolin, and the like.

The compositions of this invention are normally solid in the sense that at typical room temperatures and pressures the compositions are in a solid state as compared to a liquid state. The solid character of the composition results from both polymers having a sufficiently high molecular weight to be a solid.

The blends of this invention are characterized by extremely desirable interfacial adhesion between the copoly(phenylene sulfide) and poly(aryl sulfone). Interfaced adhesion is an important property of a blend of two polymers because it governs the strength of the blended material. When the interfacial adhesion is high, the blends can withstand higher stress before failure for any given morphology.

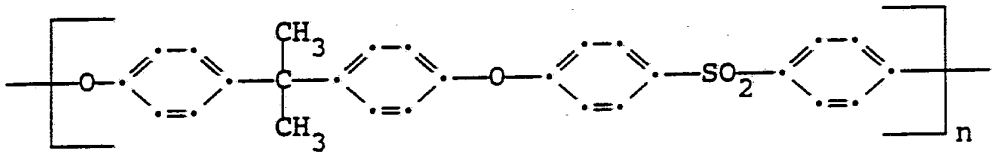
The following examples are used to describe the invention and should be taken as illustrative and not restrictive.

Example 1

This example illustrates the enhanced interfacial adhesion associated with the blends of this invention.

A copoly(phenylene sulfide) was prepared by the melt phase reaction of sulfur and p-di-iodobenzene, as described in U.S. Patents 4,786,713 and 4,792,600. The value of x was estimated to be 0.10 as determined by elemental analysis. The melt viscosity of copoly(phenylene sulfide) at 300°C at 25 Sec^{-1} shear rate was 5000 poise. Properties of the product included a melt viscosity of 5000 poise at 300°C and 25 rad/sec, a glass transition temperature of 89°C and an estimated disulfide content of 10 mol %.

A blend was prepared which contained 50 weight % of the copoly(phenylene sulfide) in powdered form and 50 weight % of a powdered poly(aryl sulfone) corresponding to the following structure



where n is at least 20.

The blend was dried for 12 hours at 120°C in a vacuum oven. The dried blend was melt blended in an extruder at 330°C. The melt blend was coarsely ground to less than 3 mm particle size and compression molded films were prepared at 300°C.

The film was cryogenically fractured in liquid nitrogen and the fracture surface morphology was determined using a scanning electron microscope. A scanning electron micrograph of the cryogenically fractured surface clearly shows good interfacial adhesion between the two phases.

Example 2

This example illustrates the poor interfacial adhesion associated with blends of poly(phenylene sulfide) and poly(aryl sulfone).

Example 1 was repeated except that a commercially available poly(phenylene sulfide) was used in place of the copoly(phenylene sulfide). The poly(phenylene sulfide) had a melt shear viscosity of 11,740 poise at 300°C and 25 sec^{-1} shear rate.

A scanning electron micrograph of the fractured surface clearly indicates very poor interfacial adhesion between the two phases.

Example 3

This example illustrates the enhanced interfacial adhesion associated with the blends of this invention.

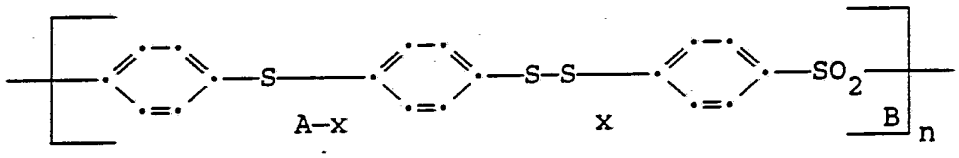
Example 1 was repeated except that the amount of poly(aryl sulfone) was 10% and the amount of copoly(phenylene sulfide) was 90%.

A scanning electron micrograph of the fractured surface clearly indicates very poor interfacial adhesion between the two phases.

Example 4

This example illustrates the enhanced interfacial adhesion associated with the blends of this invention.

A three component composition was prepared containing a poly(aryl sulfone), a copoly(phenylene sulfide) and a poly(cophenylene sulfide phenylene sulfone) corresponding to the following structure



wherein A is in the range of 0.95 to 0.05, B is in the range of 0.05 to 0.95 and x is in the range of 0.001 to 0.5 and n is at least 30.

The poly(cophenylene sulfide phenylene sulfone) was prepared in accordance with the disclosure of U.S. 4,786,713 using the following procedure. 19.5 g (0.61 moles) sulfur, 102.5 g (0.31 moles) 1,4-diiodobenzene, and 142.9 g (0.30 moles) p,p'-diiododiphenyl sulfone were introduced into a 500 mL 3-neck round-bottom flask. The melt is stirred through the center neck via a vacuum adapter and stirrer seal, using a stainless steel stirrer shaft and blade. One side neck is fitted with a 350 mm (length) Vigreaux column topped with a vacuum-jacketed takeoff head with a thermal well inserted in the top. The column, head, and takeoff is wrapped with an electric heat tape and then fiberglass tape. The column set-up is heated to approximately 100°C. the column is connected to a 500 mL 2-neck round-bottom blask which is cooled with dry ice for condensation of the volatiles. The other side neck is used as an air inlet. The air flow was maintained at 0.00283m^3/h. The reaction is started at 200 torr and 230°C for 1.25 h, then the temperature is increased to 240°C for 0.5 h, then 250°C for 1.75 h. The pressure is then decreased as follows: 175 torr for 0.25 h, 150 torr for 0.25 h, 125 torr for 0.25 h, 100 torr for 0.25 h, 60 torr for 0.25 h, and 30 torr for 0.25 h. Then the pressure is reduced to 0.5 torr via a vacuum pump for the remainder of the reaction. After one hour at 0.5 torr and 250°C, the temperature is raised to 300°C for 1 h. The

resulting copolymer was an amorphous, high viscosity material with a Tg of 147.5°C by DSC.

The three polymers are prepared into the admixture following the procedure of Example 1.

A scanning electron micrograph of the cryogenically fractured surface clearly shows good interfacial adhesion between the two phases.

CLAIMS

1. A composition comprising an admixture of
(A) from 99 to 1 weight percent, based on the weight of the admixture, of a copoly(arylene sulfide) corresponding to the structure

$$[\ (-A-S-)_{1-x}(-A-S-S-)_x\ ]_n$$

wherein A is a divalent substituted or unsubstituted aromatic radical, x is in the range of 0.5 to 0.001 and n is at least 25, and
(B) from 1 to 99 weight percent, based on the weight of the admixture, of a poly(arylsulfone).

2. The composition of claim 1 wherein the divalent aromatic radical is provided by diiodobenzene, diiodonaphthalene or diiodobiphenyl.

3. The composition of claim 1 wherein the divalent aromatic radical is p-diiodobenzene, m-diiodobenzene, p,p'-diiodobiphenyl, p,p'-diiododiphenyl ether or 2,6-diiodonaphthalene.

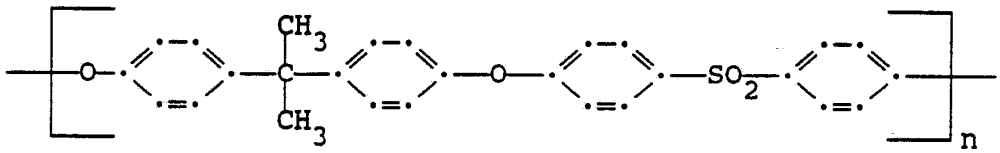
4. The composition of claim 1 wherein the amount of component (A) is in the range of 85 to 15 weight percent and the amount of component (B) is in the range of 15 to 85 weight percent.

5. A composition comprising an admixture of
(A) from 85 to 15 weight percent, based on the weight of the admixture, of a copoly(phenylene sulfide) corresponding to the structure

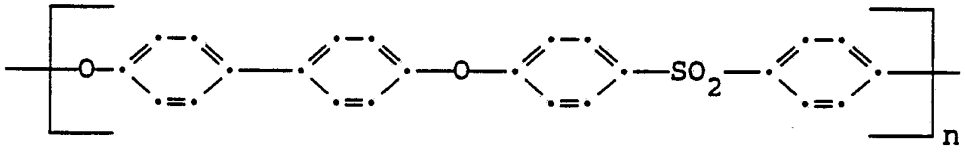
$$[\ (-A-S-)_{1-x}(-A-S-S-)_x\ ]_n$$

wherein A is a divalent phenylene radical, x is in the range of 0.5 to 0.001 and n is at least 50, and

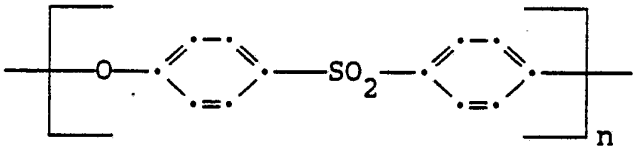
(B) from 15 to 85 weight percent, based on the weight of the admixture, of a poly(arylsulfone) corresponding to the structure



wherein n is at least 15, or to the structure

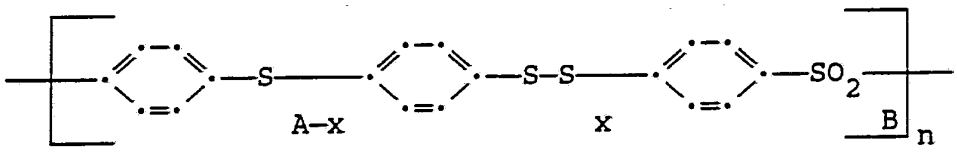


wherein n is at least 15, or to the structure



wherein n is at least 25.

6. The composition of Claim 5 wherein the composition further contains from 0.1 to 25 weight percent, based on the weight of components (A) and (B) combined, of a poly(cophenylene sulfide phenylene sulfone) corresponding to the structure



wherein A is in the range of 0.95 to 0.05, B is in the range of 0.05 to 0.95 and x is in the range of 0.001 to 0.5 and n is at least 25.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/07370

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L81/02; C08L81/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08L

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	US,A,4 021 596 (F. W. BAILEY) 3 May 1977 cited in the application see column 2, line 23 - line 63; claims 1-9,25; examples 1,2,4,7 ---	1-5
A	DATABASE WPIL Week 9047, 30 January 1991 Derwent Publications Ltd., London, GB; AN 90-351441 & JP,A,2 252 761 (DAINIPPON INK) 11 October 1990 see abstract --- -/--	1,6

° Special categories of cited documents :[10]

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"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11 NOVEMBER 1992	25. 11. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	KLIER E.K.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,A	POLYMER BULLETIN vol. 26, no. 3, August 1991, BERLIN pages 349 - 356 M. F. CHEUNG AND H. K. PLUMMER, JR 'tensile fracture morphology of polysulfone-poly(phenylene sulfide) blends'	1
A	DATABASE WPIL Week 9003, 14 March 1990 Derwent Publications Ltd., London, GB; AN 90-019559 & JP,A,1 299 872 (TORAY IND) 4 December 1989 see abstract	1-5

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9207370 SA 64367

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4021596	03-05-77	None	