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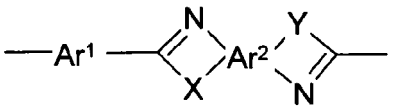
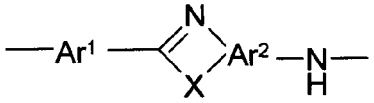
(54) Paper comprising polybenzazole or precursor thereof

(57) The invention relates to a paper comprising at least one of a fiber, pulp, fibril, floc, and fibrid containing a polybenzazole structure with a repeating unit of formula (I) and/or (II), or (III):



(I)



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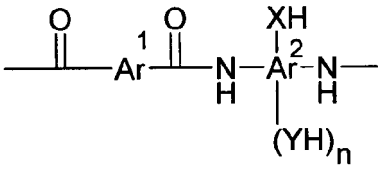

(III)

wherein Ar^1 and Ar^2 are independently an aromatic group having 4 to 12 carbon atoms, Ar1 and Ar2 have the para or meta configuration, and X and Y are the same or different and selected from O, S, and NH; n is 0 or 1. The paper can be made free of non-extractable phosphorus compound. The paper is particularly suitable for making an electrical insulation material, a honeycomb structure, or a constructive material.

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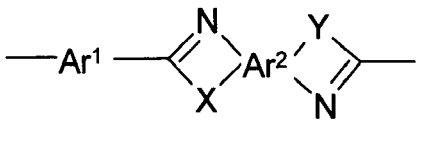
Description

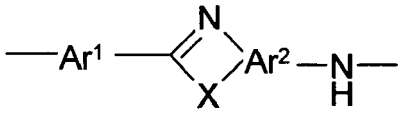
[0001] The invention relates to a paper comprising at least one of a fiber, pulp, fibril, floc, and fibrid containing a polybenzazole structure or a polybenzazole precursor structure. the invention further pertains to a method for making such papers and to the use thereof.

[0002] It has described in EP 07008742 that fiber, pulp, fibril, or fibrid having superior properties, including mechanical properties, can be obtained by a process in which an optical anisotropic dope, containing a high concentration of a high molecular weight aromatic polyamide having a substituent such as a hydroxy, thiohydroxy, or amine group in an acidic solvent, is applied using a wet air gap spinning process, a jet spinning process, or any other conventional method to obtain a fiber, pulp, fibril, or fibrid, which are then heat treated.

[0003] The present invention relates to paper made from at least one of a fiber, pulp, fibril, floc, and fibrid comprising polybenzazole having a repeating unit of formula (I) and/or (II)



(I)



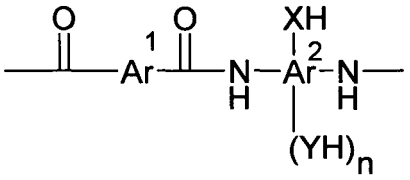
(II)

wherein Ar^1 and Ar^2 are independently an aromatic group having 4 to 12 carbon atoms, Ar^1 and Ar^2 have the para or meta configuration, and X and Y are the same or different and selected from O, S, and NH; and wherein the paper contains less than 0.15 wt% of non-extractable phosphorus compound.

[0004] The terms "para" and"meta" relate to the positions of the two amino groups or the two carbonyl groups at the aromatic ring. If Ar^2 contains more than one aromatic ring there are formally no para and meta positions, but the corresponding positions are mentioned pseudo-para and pseudo-meta positions, which are included in the definition of "para" and"meta".

[0005] The present fibers, pulp, fibrils, floc, or fibrids are manufactured by a method comprising the steps of spinning or extruding a dope and solidifying it to a coagulation liquid, and then subjecting the obtained fiber as was described in EP 07008742.

[0006] The invention also relates to a precursor paper, which as such has excellent properties and therefore can be used as such. This precursor paper contains a polybenzazole precursor having the repeating unit expressed by formula (III):

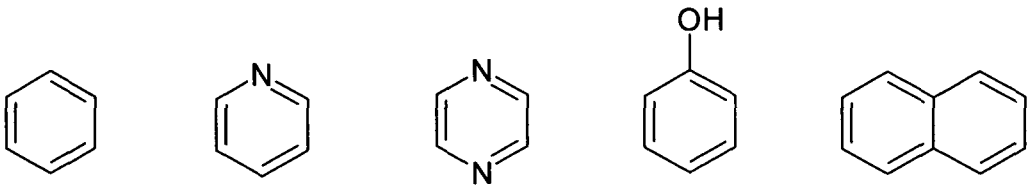


(III)

wherein Ar^1 and Ar^2 are independently an aromatic group having 4 to 12 carbon atoms, Ar^1 and Ar^2 have the para or meta configuration, X and Y are the same or different and selected from O, S, and NH, and n is 0 or 1.

[0007] Examples of Ar^1 are phenylene, naphthalenediyl, and bivalent heteroaromatic groups. Ar^1 may be substituted with hydroxy and/or halogen groups.

[0008] Ar^1 is preferably selected from



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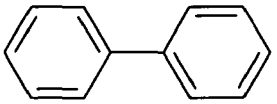
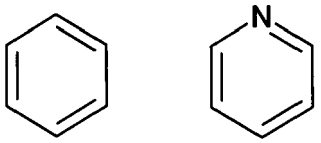


[0009] Ar^2 is a tri- or quadrivalent aromatic group with 4-12 carbon atoms. Examples of A^2 are benzenetri- or tetrayl, naphthalenetri- or tetrayl, diphenyltri- or tetrayl, and tri- or quadrivalent heterocyclic group can be listed as Ar^2. These Ar^2 moieties may be substituted with a hydroxy and/or halogen group.

[0010] Ar^2 is preferably selected from:



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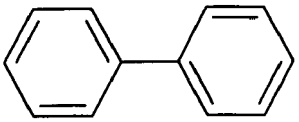
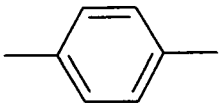


[0011] The benzene group is the most preferred Ar^2 group.

[0012] In a preferred embodiment Ar^1 is para- or meta-phenylene:



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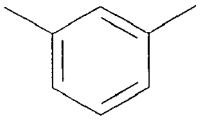
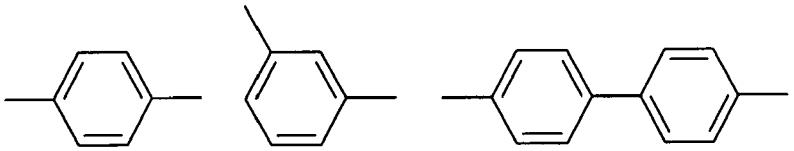
or



and Ar^2 is



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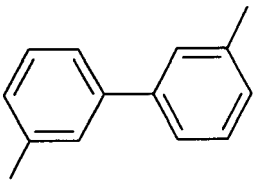
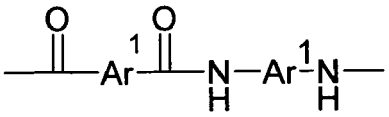


wherein X and Y are O, and the straight lines represent a bond.

[0013] In addition to the above polybenzazole the fiber may also be a copolymer containing repeating units expressed by formula (IV)



(IV)

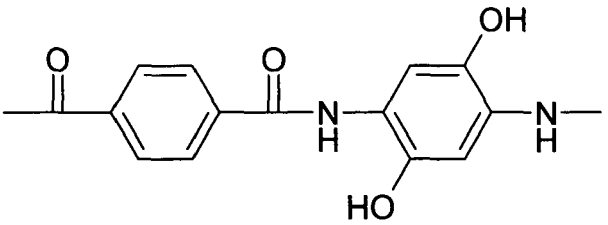
[0014] In formula (III), the Ar^1 groups have independently the previously given meanings. The preferred Ar^1 is para- or meta-phenylene.

[0015] The polybenzazole preferably comprises 40 to 100 mole% of the repeating unit expressed by formula (I) and/or (II) with 60 to 0 mole% of the repeating unit expressed by formula (IV), to a total of 100 mole%.

[0016] The polybenzazole preferably comprises 60 to 100 mole% of the repeating unit expressed by formula (I) and/or (II) with 40 to 0 mole% of the repeating unit expressed by formula (IV), to a total of 100 mole%.

[0017] Since X is an oxygen atom (-O-), sulfur atom (-S-), or imino group (-NH-), the polybenzazole which can be obtained form the polymer precursors contains imidazole, thiazole, and/or oxazole rings.

[0018] The polybenzazole precursor containing one of the following repeating units is especially preferred.



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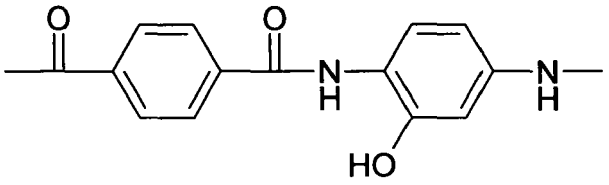

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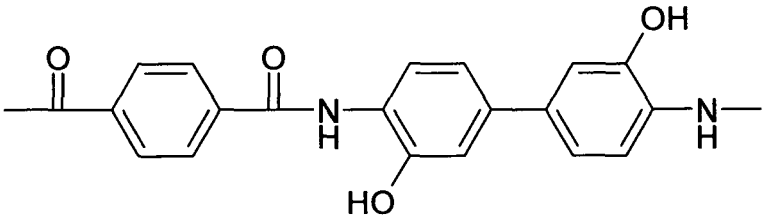

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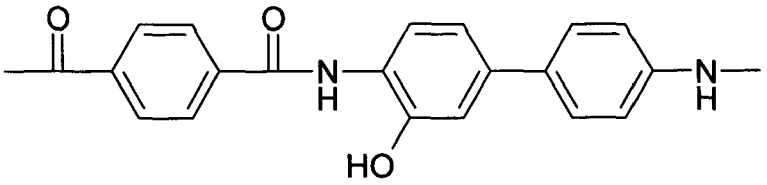

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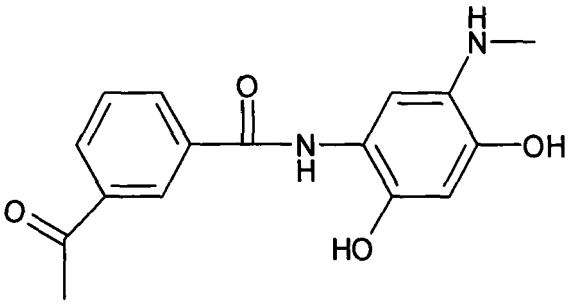

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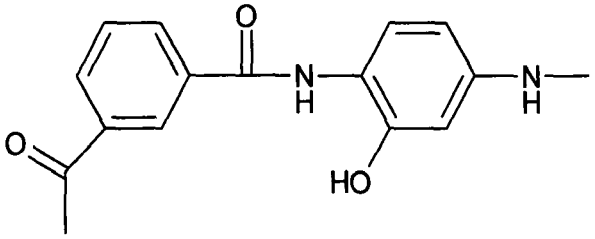


[0019] Methods for making these polymers, and for making fiber, pulp, fibril, floc or fibrid thereof are disclosed in

European patent application no. EP 07008742, which is incorporated by reference.

[0020] Although PBO paper is known in the art, i.e. as mentioned in patent US 6890636, such paper inherently contains substantial amounts of phosphoric acid which was used as spin dope for making fiber, and which cannot completely be removed. The PBO paper of this invention contains less than 0.15 wt% of non-extractable phosphorus compound (i.e. mainly phosphoric acid), preferably much less such as less than 30 ppm, and most preferably none or virtually none of phosphorus compound (when the spin dope does not contain any phosphoric acid). Because it is known that traces of phosphoric acid may decompose PBO fibrous materials, leading to substantial loss of paper strength, it may is utmost importance to make PBO paper that is free or at least substantially free of phosphoric acid, if such paper should maintain its strengths for long periods. The unique method for making the PBO paper of this invention resides in a method wherein the ring-closed PBO structure is obtained from an open precursor structure still having OH, SH, or NH_2 groups. These hydrophilic groups allow the precursor to dissolve in hydrophilic solvents such as water, alcohol, water-alcohol mixtures, and the like.

[0021] Whereas PBO can practically only be dissolved in phosphoric acid-containing spin dopes, the present precursors can form spin dopes in said hydrophilic solvents, without using any phosphoric acid. Such spin dopes will lead to fiber, pulp, fibril, floc or fibrid that is completely or virtually free from phosphorus compound. PBO paper having less than 0.15 wt% phosphorus compound is unknown. The known PBO papers have been made from PBO-polyphosphorus acid-containing spin dopes, leading to paper having (much) more than 0.15 wt% non-extractable phosphorus. Although it is usually not preferred, small amounts of phosphorus acid or other phosphorus compounds can be added to the spin dope, leading to papers having minor amounts (i.e. less than 0.15 wt%) of phosphorus. The amount of phosphorus present in the paper can easily be measured by using standard methods such as by spectroscopy or titration.

[0022] The papers of this invention may include combinations of fiber, pulp, fibril, floc or fibrid, such as fibrids and floc. The papers of the invention can be made by conventional papermaking processes, which processes allow adding common additives and auxiliary materials to the material for making paper, such as pigments, binders, silicates, fillers, and other additives. The paper such obtained may be processed further such as by applying known calendaring methods to further enhance the density of the paper.

[0023] The term "fibrids" refers to non-granular film-like particles. The fibrids have an average length of 0.2 to 1 mm with a length-to-width aspect ratio of 5:1 to 10:1. The thickness dimension is on the order of a fraction of a micron. Such fibrids, when fresh, are used wet and are deposited as a binder physically entwined about the floc component of the paper. Fresh fibrids and previously-dried fibrids can be used in paper of this invention.

[0024] The term "floc" refers to short fibers, typically having a length of 2 to 12 mm and a linear density of 1-10 decitex. The floc can be fresh or it can be previously-dried. If fresh, it has not before been used in any product.

[0025] Paper pulp may comprise floc and fibrids, generally, in amounts of about 50-60%, by weight, fibrids and 40-50%, by weight, floc. Even after comminution and milling, the floc in aramid paper pulp is bound, to some extent, by the fibrids. The fibrids, being in a dried state, are bound together or collapsed and less useful as binder material than the fresh, never-dried, fibrids; but, due to their random, rigid, irregular, shape, contribute an increased porosity to the final paper structure. For purposes of this invention, those fibrid and floc components taken from dried papers may be called previously-dried fibrids and previously-dried floc.

[0026] Dried paper sheets containing polybenzazole precursor can also be processed through a high speed milling machine, such as a turbulent air grinding mill known as a Turbomill or an Ultra-Rotor, and then wet refined. Turbulent air grinding mills are preferred for comminuting papers which have been calendered; but the grinding mills result in slightly shortened fiber lengths. Paper of this invention using paper pulp with shortened fiber lengths exhibits slightly reduced wet strength and a tendency to worsen paper machine continuity.

[0027] The paper made from the polybenzazole precursor material can be used as such. It has excellent properties as will further be demonstrated in the experimental part. However, the properties of this paper can easily be changed or improved by functionalizing at least part of the free XH and YH groups, such as OH groups. These free groups are able to react with monomers and polymers having reactive groups, such as esters, isocyanates, epoxides, and other functionalizing agents to give a covalent bond between X and/or Y and the functionalizing agent. If part of the free XH and YH groups is functionalized these papers can also be heat treated to convert the polymer precursor by a cyclizing process to ring-closed PBO polymers, thereby obtaining functionalized PBO paper. Because the polymer precursor has been synthesized and spun from solutions that may be free from phosphorus compounds, the PBO obtained can also be free of phosphorus compounds. It is a further advantage that it is no longer required to make the paper from almost insoluble PBO polymers, but the papermaking process can be performed with readily soluble polymer precursors, and conversion to PBO takes place after formation of the paper.

[0028] In general the papers from this invention exhibit lower porosity than PPTA papers making them very suitable for electrical applications such as in electrical insulation material. The papers are further suitable for application in honeycomb structures and in constructive materials.

[0029] The papers of the present invention, both for PBO precursor-containing papers and PBO papers, have a much higher strength than known papers, as shown by EAB (elongation at break) and TI (tenacity index) data. For instance,

the present papers are superior to PPTA paper and even to Nomex®, which is considered the strongest paper known until now.

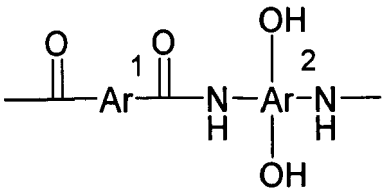
[0030] The extreme strength of the present papers makes it possible to produce extreme thin papers. The papers of this invention also have superior heat stability compared to PPTA paper and Nomex®.

[0031] Because of the unusual strength of the present papers, papers having a grammage between 1 and 16 g/m^2 can be made. The term "grammage" is a metric measure of paper weight based on the same square meter sheet of paper, regardless of paper grade.

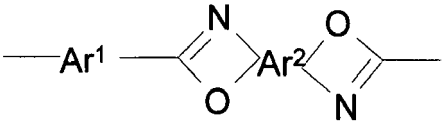
[0032] The present invention will be explained more specifically by the following embodiments. However, the present invention is not limited to these embodiments.

General:

[0033] These results were obtained with the polymer precursor having the following repeating unit:



and with the corresponding ring closed polymer having the repeating unit:



wherein Ar^1 = para-phenylene and Ar^2 = diphenylene

[0034] Abbreviations:

NMP = N-metylpyrrolidone
DHB = dihydroxybenzidine (4,4'-diamino-3,3'-dihydroxydiphenyl)
TDC = terephthaloyl dichloride
PPD = para-phenylenediamine
PPTA = para-phenyleneterephthalamide

Example 1

Polymerization to polybenzoxazole precursor

[0035] 2.25 L of NMP/$CaCl_2$ and 1.75 L of NMP together with pre-dried DHB (140 °C, vacuum, 24 h) were charged into a 10 L Drais reactor and stirred for 30 minutes to let the DHB dissolve. After cooling to 5 °C, TDC was added while continuously stirring (250 rpm). After 50 minutes a sample was taken, 1.8 L of NMP were added. The mixture was stirred for 30 min, another sample was taken and again 1.8 L of NMP were added. The mixture was stirred for 30 min and the reactor was emptied through a bottom valve. By applying this procedure, the first sample had a polymer concentration of 7.4%, the second sample (after dilution with NMP) had a concentration of 5% and the final product had a polymer concentration of 4%. The relative viscosity of the reaction product was 3.43.

[0036] The polymerization procedure for the second batch was similar, except that after 60 minutes a sample was taken and 4.0 L of NMP were added. The mixture was stirred for 30 min and then emptied. By applying this procedure, the first sample had a polymer concentration of 7.4% and the final product had a polymer concentration of 4%. The relative viscosity of the reaction product was 3.06.

[0037] The polymerization batches were mixed prior to spinning.

Comparative example 1

[0038] Polymerization of PPTA para-phenyleneterephthalamide was carried out using a 160 L Drais reactor. After sufficiently drying the reactor, 64 L of NMP/$CaCl_2$ with a $CaCl_2$ concentration of 2.5 wt% were added to the reactor. Subsequently, 1522 g of PPD were added and dissolved at room temperature. Thereafter the PPD solution was cooled to 5 °C and 2824 g of TDC were added. After addition of the TDC the polymerization reaction was continued for 45 min. Then the polymer solution was neutralized with a calcium oxide/NMP-slurry (780 g of CaO in NMP). After addition of the CaO-slurry the polymer solution was stirred for another 30 min. This neutralization was carried out to remove the hydrochloric acid (HCl), which is formed during polymerization. A gel-like polymer solution was obtained with a PPTA content of 4.5 wt% and having a relative viscosity of 3.0 (in 0.25% H_2SO_4). This product has an etarel (η_{rel}) of 2.4 and a polymer concentration of 3.6% and was used to spin fibrids as well as pulp. Water was used as coagulant.

Example 2

Fibrid and pulp making

[0039] The solutions of Example 1 and Comparative Example 1 were spun through a jet spinning nozzle (spinning hole 500 μm) at 20 Uh. Water was added through a ring-shaped channel flowing perpendicular to the polymer flow. During spinning the polymer flow was kept constant while the coagulant pressure was changed for the different samples in order to vary the SR (°SR) of the product.

Pulp spinning

[0040] The solutions of Example 1 and Comparative Example 1 were spun into pulp through a 1 hole jet spinning nozzle (spinning hole 350 μm). The solution was spun into a zone of lower pressure. An air jet was separately applied perpendicularly to the polymer stream through ring-shaped channels to the same zone were expansion of air occurred. Thereafter, the pulp was coagulated with water in the same zone by means of applying a coagulant jet through ring-shaped channels under an angle in the direction of the polymer stream.

[0041] To spin the pulp with different SR values (°SR) the air pressure was kept constant while the polymer flow was varied. After spinning all samples were washed with water.

[0042] The process and property data of fibrids and pulp obtained in Example 2 are given in Table 1:

Table 1

		Process parameters					Properties				
Sampl e	Polymer solution	Product type	Polymer solution Flow (Uh)	Coagulant pressure (bar)	Coagulant flow (Uh)	Airflow (Nm^3/h)	$LL_{0.25}$	Fines(%)	SR Value (°SR)	SSA (m2/g)	Dry Solids (%)
A	Example1	pulp	6		50	12	0.58	43.3	63	0.6	5.3
B	Example1	fibrid	20	50			0.72	25	67	0.5	7.3
C	CompEx1	fibrid	20	30			0.84	25	42	2.2	5.6
D	CompEx1	fibrid	20	50			0.74	26.3	65	2.6	4.8
E	CompEx1	pulp	6		50	12	0.55	49.9	68	5.6	7.5
F	CompEx1	pulp	18		50	12	0.62	42.7	46	3.9	6.9

Example 3

Paper making from fibrids

[0043] Handsheets from 100% fibrids of samples A1 and B1-B4 and comparative examples D1-D4 and E1 with different grammage were made on a Rapid Kothen machine. The dewatered sheets were dried between two blotting papers under vacuum (95 °C, -1000 mbar, 20 min). Paper data are given in Table 2.

[0044] Notice the lower calliper (paper thickness) and higher densities for the papers of the invention in comparison to the reference papers. TI (Tensile Index) is 3-5 times as high for the papers of the invention than for the pulp-based reference papers when compared at the same grammage. EAB is also higher for the papers of the invention.

Table 2: Properties of paper samples from fibrid

Paper Sample	Grammage (g/m^2)	Calliper (mm)	Density (g/cm^3)	EAB (%)	TI (Nm/g)
B1	99	0.168	0.59	4.3	85.2
B2	50	0.115	0.44	3.6	75.3
B3	29	0.073	0.39	3.7	72
B4	16	0.058	0.28	2.5	41.6
D1	110	0.284	0.39	1.7	28.3
D2	52	0.193	0.27	1.7	19
D3	31	0.131	0.23	1.1	14.1
D4	16	0.092	0.17	1.6	8.1

Example 4

Paper making from pulp

[0045] Handsheets from 100% pulp of samples A and E with a grammage of around 100 g/m^2 were made on a Rapid Kothen machine using the same procedure as Example 3. Paper data are given in Table 3.

Table 3: Properties of paper samples from pulp

Paper Sample	Grammage (g/m^2)	Calliper (mm)	Density (g/cm^3)	EAB (%)	TI (Nm/g)
A1	110	0.265	0.415	1.5	18.8
E1	117	0.296	0.395	1.05	9.5

Example 5

Heat treatment of papers

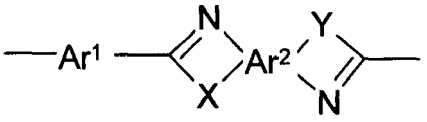
[0046] To convert the above polybenzazole precursor paper to the polybenzazole paper a heat treatment was performed under an inert atmosphere The procedure was as follows: The samples were enclosed in an oven under an nitrogen flow and heated with a heating rate of 10 °C/min. When the temperature of 440 °C was reached the samples were immediately taken out of the oven. Property data of the samples before and after heat treatment are given in Table 4. IR spectra of the samples were recorded on the Varian FTS-575c Infrared spectrometer equipped with the Thunderdome ATR accessory. The spectra confirmed conversion to a polybenzoxazole paper with a conversion factor >0.95.

[0047] TGA experiments were carried out by means of a Setaram TGA/DSC 111, under nitrogen gas. The paper samples were first cut into pieces and then put in Platinum (open) cells. The sample weight that was used was between 10 and 20 mg. The samples were heated from 20 °C to 700 °C. The decomposition temperature $Td_{5\%}$ is the temperature at which 5% weight loss based on TGA thermogram is obtained under these conditions.

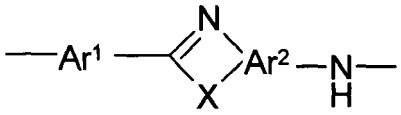
Paper Sample	Type	Heat Treated	Grammage (g/m^2)	Calliper (mm)	Density (g/cm^3)	EAB (%)	TI (Nm/g)	$Td_{5\%}$ °C
B5	fibrid paper	No	102.2	0.181	0.56	3	70	630
B6	fibrid paper	Yes	99.8	0.151	0.66	3.6	80	625
A1	pulp paper	No	110	0.265	0.42	1.5	18.8	630
A2	pulp paper	Yes	118	0.207	0.57	1.8	16.8	625
D2	fibrid paper	No						540
D3	fibrid paper	Yes						

Claims

1. A paper comprising at least one of a fiber, pulp, fibril, floc, and fibrid containing a polybenzazole structure with a repeating unit of formula (I) and/or (II)



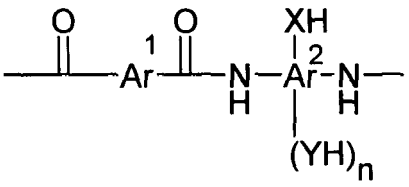
(I)



(II)

wherein Ar^1 and Ar^2 are independently an aromatic group having 4 to 12 carbon atoms, Ar1 and Ar2 have the para or meta configuration, and X and Y are the same or different and selected from O, S, and NH; and wherein the paper contains less than 0.15 wt% of non-extractable phosphorus compound.

2. A paper comprising at least one of fiber, pulp, fibril, floc, and fibrid having a polybenzazole precursor structure containing the repeating unit expressed by formula (III):



(III)

wherein Ar^1 and Ar^2 are independently an aromatic group having 4 to 12 carbon atoms, Ar^1 and Ar^2 have the para or meta configuration, X and Y are the same or different and selected from O, S, and NH, and n is 0 or 1.

3. The paper of claim 2 wherein at least part of XH and/or YH is functionalized.

4. The paper of any one of claims 1-3 having a grammage from 1 to 16 g/m^2.

5. The paper of any one of claims 1-4 comprising a mixture of at least one of fiber, pulp, fibril, floc, and fibrid containing a polybenzazole structure of formula (I) and/or (II) or a polybenzazole precursor structure of formula (III), and PPTA fibrid.

6. A method for making the paper of claim 1 comprising heating the paper of claim 2 or 3 under an inert atmosphere

at a temperature allowing cyclization of the polybenzazole precursor having formula (III) to the polybenzazole comprising the structure of formula (I) and/or (II).

7. A method for making the paper of claim 2 or 3 comprising applying a conventional papermaking process using at least one of fiber, pulp, fibril, floc, and fibrid having the polybenzazole precursor structure IV, optionally followed by one or more of a calendering step, heating step, drying step, and functionalization step.

8. An electrical insulation material comprising the paper of any one of claims 1-5.

9. Use of the paper of any one of claims 1-5 for making an electrical insulation material, a honeycomb structure, or a constructive material.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 01 7825

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	4 April 2008	Naeslund, Per

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