



(51) International Patent Classification:

D21H 27/00 (2006.01) *D21H 21/00* (2006.01)
D21H 13/26 (2006.01) *D21H 21/14* (2006.01)
D21H 15/10 (2006.01) *C08K 3/00* (2006.01)
D21H 17/49 (2006.01) *C08K 7/02* (2006.01)
D21H 17/00 (2006.01) *C08K 9/04* (2006.01)

(21) International Application Number:

PCT/US2014/011001

(22) International Filing Date:

10 January 2014 (10.01.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

13/743,779 17 January 2013 (17.01.2013) US

(71) Applicant: **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).

(72) Inventors: **JAYCOX, Gary, Delmar**; 837 Brintons Bridge Road, West Chester, PA 19382 (US). **DOWNEY, Jeffrey, S.**; 4491 Larry York Road, Battersea, ON N0H 1H0 (CA).

(74) Agent: **STRICKLAND, Frederick, D.**; E. I. Du Pont De Nemours And Company, Legal Patent Records Center, Chestnut Run, Plaza 721/2340, 974 Centre Road, Po Box 2915, Wilmington, DE 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: ELECTRICALLY CONDUCTIVE PULP AND METHOD OF MAKING

(57) Abstract: An electrically conductive pulp suitable for use as a reinforcement comprises from 60 to 96 weight percent of fibers of aromatic polyamide, aromatic copolyamide or mixtures thereof and from 4 to 40 weight percent of conductive material coated onto the fibers wherein the conductive material comprises (i) a polymer of aniline, or (ii) a random copolymer formed from aniline and one or more substituted aniline co-monomers that exist in the protonated emeraldine salt form.



TITLE OF INVENTION

5

ELECTRICALLY CONDUCTIVE PULP AND METHOD OF MAKING**BACKGROUND**10 1. Field of the Invention

This invention pertains to electrically conductive pulp, a method of making the pulp and compounds formed during the making of the pulp.

2. Description of Related Art

15 Short length para-aramid fibers in pulp form are well suited as matrix reinforcing materials and find increasing application in various mechanical rubber goods such as tires, belts and hoses. The non-conductive behavior of para-aramid pulp necessitates the use of carbon black particles as an additional additive in rubber formulations when
20 electrical conductivity properties are required. Conductive carbon blacks are required to dissipate static charge build-up that naturally occurs in a rolling tire. Unfortunately, the unwanted aggregation of carbon black particles within the tire "matrix" leads to heat build-up and other deleterious effects that increase tire rolling resistance. There is therefore a
25 need to provide para-aramid type pulp in an electrically conductive form and eliminate the addition of carbon black in the rubber formulation.

United States Patent 6,436,236 to Hartzler describes an electrically-conductive pulp of sulfonated polyaniline blended with para-aramid wherein the para-aramid is a continuous phase in the pulp and the
30 sulfonated polyaniline is a discontinuous phase.

United States Patent 5,882,566 to Hsu describes a method to make electrically conductive high strength and high modulus para-aramid fibers

by spinning, from a lyotropic spin solution, filaments comprising para-aramid and sulfonic acid in situ ring-substituted polyaniline.

SUMMARY OF THE INVENTION

5 This invention pertains to an electrically conductive pulp suitable for use as a reinforcement comprising from 60 to 96 weight percent of fibers of aromatic polyamide, aromatic copolyamide or mixtures thereof and from 4 to 40 weight percent of conductive material coated onto the fibers wherein the conductive material comprises

- (i) a polymer of aniline, or
- 10 (ii) a random copolymer formed from aniline and one or more substituted aniline co-monomers that exist in the protonated emeraldine salt form.

DETAILED DESCRIPTION

15 Pulp

Pulp is a highly fibrillated fiber product that is manufactured from yarn by chopping the yarn into staple then mechanically abrading in water to partially shatter the fibers. Para-aramid fibers are particularly suited for the manufacture of pulp due to their high tenacity and fibrillar morphology.

20 United States Patents 5,084,136 and 5,171,402 describe such para-aramid pulps. Para-aramid fiber products are available under the tradename Kevlar® from E. I. du Pont de Nemours and Company, Wilmington, DE (DuPont). Para-aramid fibers are converted into pulp to give a large increase in surface area as fibrils with diameters as low as 0.1

25 micrometer are attached to the surface of the main fibers, which are typically 12 micrometers in diameter. Typically, para-aramid pulp has a specific surface area of from 7 to 11 m²/g although values in the range of 4.2 to 15 m²/g have been reported. If they are to be highly dispersible in water or different matrices, para-aramid pulp must be kept moist to

30 prevent the fibrillar morphology from collapsing. Preferably, the pulp fiber length is in the range of from 0.5 to 1.1 mm or even in the range of from 0.6 to 0.8 mm when determined as a Kajaani weight average length. Para-

aramid fibers and pulps can be converted into micropulps by wet milling to increase their surface area as described in United States Patent Publication 2003/0114641 A1. Typically, micropulp has a specific surface area of from 15 to 80 m²/g with a fiber length of from 10 to 100
5 micrometers.

Para-aramid pulps are used as fillers in elastomer compounds to modify their tensile properties. A large application is in natural rubber for tire reinforcement. The moist pulps are dispersed into water and mixed with elastomer latexes then coagulated to give concentrated
10 masterbatches such as Kevlar® Engineered Elastomer (EE). The EE masterbatches contain the pulp in a highly dispersed state that can be compounded into bulk elastomer to give the desired level of pulp modification. This process is further described in United States Patents 5,830,395 and 6,068,922. Dry pulps are difficult to disperse directly into
15 elastomers and remain agglomerated.

Aromatic Polyamide

Para-aramid, an aromatic polyamide, is a suitable polymer for the fibers of the pulp. The term "aramid" means a polyamide wherein at least
20 85% of the amide (-CONH-) linkages are attached directly to two aromatic rings. Suitable aramid fibers are described in Man-Made Fibres – Science and Technology, Volume 2, Section titled Fibre-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968.

A preferred para-aramid is poly (p-phenylene terephthalamide)
25 which is called PPD-T. By PPD-T is meant a homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and, also, copolymers resulting from incorporation of small amounts of other diamines with the p-phenylene diamine and of small amounts of other diacid chlorides with the terephthaloyl chloride. As a
30 general rule, other diamines and other diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction. PPD-T, also means

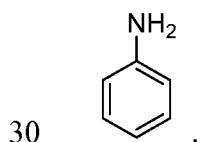
copolymers resulting from incorporation of other aromatic diamines and other aromatic diacid chlorides such as, for example, 2, 6-naphthaloyl chloride or chloro- or dichloroterephthaloyl chloride or 3, 4'-diaminodiphenylether.

5 Additives can be used with the aramid and it has been found that as much as 10 percent or more, by weight, of other polymeric material can be blended with the aramid. Copolymers can be used having as much as 10 percent or more of other diamine substituted for the diamine of the aramid or as much as 10 percent or more of other diacid chloride substituted for
10 the diacid chloride or the aramid.

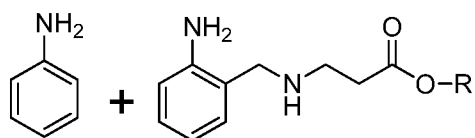
Another suitable fiber is one based on aromatic copolyamide prepared by reaction of terephthaloyl chloride (TPA) with a 50/50 mole ratio of *p*-phenylene diamine (PPD) and 3, 4'-diaminodiphenyl ether (DPE). Yet another suitable fiber is that formed by polycondensation
15 reaction of two diamines, *p*-phenylene diamine and 5-amino-2-(*p*-aminophenyl) benzimidazole with terephthalic acid or anhydrides or acid chloride derivatives of these monomers.

Conductive Material

20 Polyamide pulp as described above can be rendered electrically conductive by coating the fibers of the pulp with a conductive material produced by the oxidative polymerization of aniline such that from 60 to 96 weight percent of the pulp are fibers and from 4 to 40 weight percent of the pulp is electrically conductive coating, based on the total weight of fibers
25 plus coating. Preferably, the coating material comprises a polymer of aniline or a random copolymer formed from aniline and one or more substituted anilines that exist in the protonated emeraldine salt form. This aniline polymer or copolymer is also referred to as PANI. In some embodiments, the aniline is the unsubstituted parent compound:



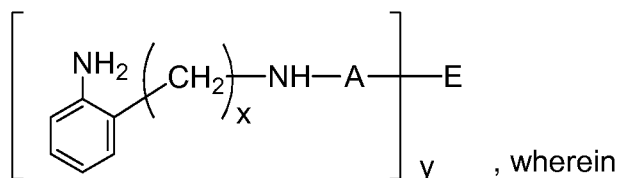
In some other embodiments, the aniline is a mixture of:



where R contains one or more sites of unsaturation or a mixture of aniline and one or more substituted polyfunctional aniline co-monomers that can serve to crosslink the conductive polyaniline coating.

5

Suitable polyfunctional aniline co-monomers include:

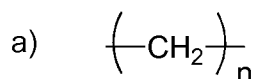


(i) x is an integer of 1 to 4,

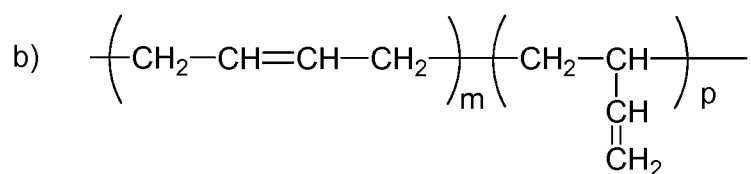
(ii) y is an integer of 2 to 4,

(iii) A is $-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}-$ or $-\text{C}(=\text{O})-$, and

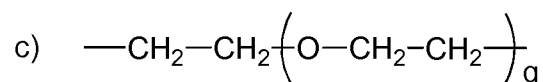
(iv) E is selected from the group consisting of:



when $y = 2$ and where n is an integer from 1 to 200,



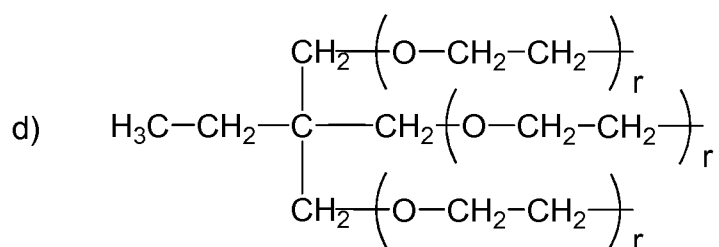
when $y = 2$ and where $m + p$ is an integer from 1 to 200,



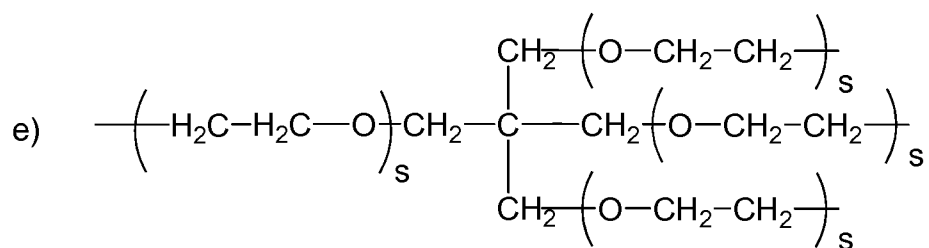
when $y = 2$ and where q is an integer from 1 to 20,

5

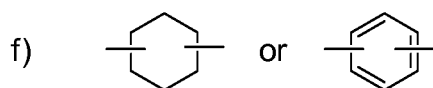
10



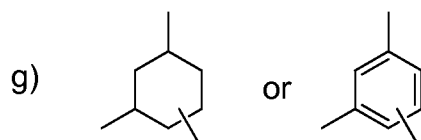
when $y = 3$ and where r is an integer from 0 to 5,



when $y = 4$ and where s is an integer from 0 to 5,



when $y = 2$, and



when $y = 3$.

Other suitable aniline derivatives for use as co-monomers in processes to give random PANI copolymers with pendant functional groups are those with substitution in the ortho position. Chemical substituents can include "hydrophilic" groups that aid in the aqueous dispersibility of the PANI-pulp complex.

In one embodiment of an aniline co-monomer mixture, the parent aniline is used in an amount of at least 90 mol % and the substituted aniline(s) used in an amount of no greater than 10 mol %.

Method of Making the Electrically Conductive Pulp

A method of making an electrically conductive fibrous pulp suitable for use as a reinforcement wherein the fibers are aromatic polyamide, aromatic copolyamide or mixtures thereof, comprises the steps of

- (i) forming a suspension of pulp in an aqueous acid dopant,
- (ii) adding aniline or aniline and at least one substituted aniline co-monomer to the suspension such that the weight percent ratio of the amount of aniline, or the amount of aniline and substituted aniline co-monomers, to the amount of pulp is in the range of from 4 to 40,
- (iii) adding an initiator to the dispersion in the amount of one molar equivalent relative to aniline, or one molar equivalent relative to aniline and substituted aniline co-monomers, to effect polymerization,
- (iv) stirring the pulp suspension for a sufficient time to ensure precipitation of the desired amount of aniline polymer or random copolymer onto the surface of the pulp,
- (v) filtering the suspension to isolate the coated pulp product in a first filtration step,
- (vi) washing the coated pulp product with additional aqueous acid dopant solution, and
- (vii) isolating the washed coated pulp product in a second filtration step.

Optionally, the polyaniline coated pulp product of step (vii) may be dried under vacuum to remove water and other volatile by-products. In one embodiment, the sequence of steps (ii) and (iii) above may be reversed.

5 When the oxidative polymerization reaction described above is carried out in the presence of dispersed para-aramid or co-polyamide pulp, the pulp fibers in the aqueous medium become coated with the conductive polyaniline (PANI) polymer. Surprisingly and unexpectedly, the modified pulp remains well dispersed even when relatively high loadings of PANI
10 (up to 40 wt% relative to pulp) are deposited out in this manner. The relative amounts of PANI deposited onto the fiber surfaces can be controlled by adjusting the starting aniline monomer - to - pulp ratio. Preferably, the PANI polymer is present in an amount of from 4 to 40 weight percent of the total weight of coated pulp. By varying the amount of
15 aniline monomer relative to the amount of suspended pulp, the "thickness" of the conducting PANI layer on the pulp can be controlled.

 In some embodiments, the surface of the para-aramid pulp can be partially hydrolyzed prior to forming a suspension in an aqueous acid dopant. Preferably, this partial hydrolysis is carried out in 10% sodium
20 hydroxide for 1 hour to 24 hours at room temperature followed by washing to a pH 7 and generates reactive amine sites on the fiber surfaces via hydrolysis of some individual polyaramide chains. It is believed that the hydrolysis reaction roughens up the polyaramide surface, thus enhancing the adsorption of the polyaniline layer to the substrate. The newly formed
25 free amine sites can also serve as "starting points" for the subsequent aniline polymerization reaction, resulting in PANI chains that are now covalently tied, as opposed to just physically bound, to the fiber surfaces.

 The acid dopant is a strong acid such as hydrochloric acid, dodecyl benzene sulfonic acid or camphorsulfonic acid. Other protonic acids are
30 also suitable.

 In some embodiments, a preferred polymerization initiator is ammonium persulfate, potassium persulfate or hydrogen peroxide or mixtures thereof.

In another embodiment, the polymerization reaction involving aniline or involving a mixture of aniline with at least one other substituted aniline co-monomer is initially run in the acid dopant medium devoid of suspended pulp to generate discrete particles of PANI or the PANI copolymer. A suspension of pulp is then added to this mixture. In some
5 embodiments, the pulp suspension is added after about an hour. The polymerization reaction continues to occur, with the new PANI that is formed depositing out onto the pulp surfaces. Many of the particles that were generated earlier tend to remain “free” and are physically mixed with
10 the coated pulp product.

Composite Material

Electrically conductive pulp as described above may be used as a component of a composite material.

15 In one embodiment, the pulp is formed into a nonwoven sheet such as a veil or paper in which the fibers are randomly oriented. This sheet is then combined with a matrix resin and/or an adhesive. Other types of reinforcing fabrics or tapes may also be present.

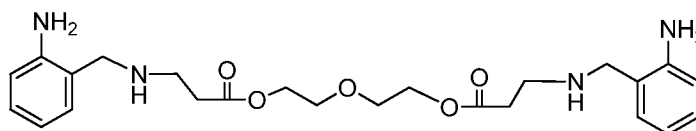
 In another embodiment, the pulp may be blended with a matrix
20 resin or adhesive.

EXAMPLES

Examples 1-3 describe the preparation of aniline co-monomers that
25 **are suitable for forming crosslinked PANI compositions.**

Example 1

The following example details the synthesis of a water soluble aniline co-monomer containing two polymerizable aniline end groups.



Aniline co-monomer 1

2-Aminomethyl aniline (22.8 g, 0.187 mol) dissolved in tetrahydrofuran (100 mL) was added dropwise over a 50 minute period to a chilled (0 °C) solution of diethylene glycol diacrylate (20.0 g, 0.093 mol; 0.187 mol reactive acrylate groups) in tetrahydrofuran (100 mL). After the addition was complete, the light yellow reaction mixture was allowed to warm to room temperature and then stirred for an additional 72 hour period. The reaction mixture was concentrated in vacuo to give a light orange colored oil.

10

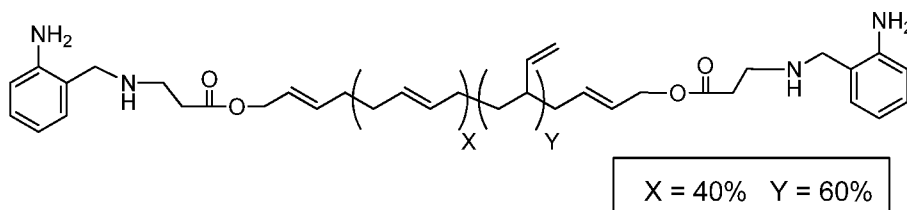
Analysis of the product by ^1H NMR spectroscopy (CDCl_3) showed a complete absence of proton resonances for starting acrylate end groups (5.7 – 6.5 ppm) and the presence of new signals at 6.6 and 7.1 ppm (aromatic ring; C_6H_4), 5.9 ppm (aromatic amine; $\text{H}_2\text{N}-\text{C}_6\text{H}_4$) and 3.8 ppm (methylene; $\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-$) due to the newly placed, terminal aniline moieties. FTIR spectroscopy (neat) confirmed the inclusion of primary and secondary amine groups in the product, with new resonances appearing in the IR spectrum near 3422 and 3316 cm^{-1} .

15

20 Example 2

The following example details the synthesis of an aniline co-monomer fitted with two polymerizable aniline end groups and an internal polybutadiene linker containing double bond sites that can co-cure with rubber during the vulcanization step.

25



Aniline co-monomer 2

30

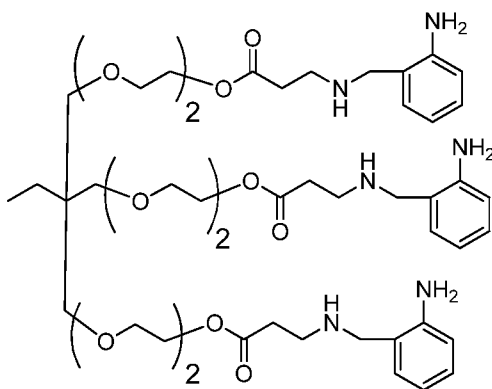
2-Aminomethyl aniline (6.75 g, 0.055 mol) dissolved in tetrahydrofuran (80 mL) was added dropwise to a solution of Sartomer CN-307 polybutadiene di-acrylate (36 g, 0.055 mol reactive acrylate groups) in tetrahydrofuran (200 mL) over a 10 minute period at room temperature. After the addition
5 was complete, the light tan reaction mixture was stirred for an additional 48 hour period and then concentrated in vacuo to give a viscous, dark-brown oil. The crude product was redissolved into chloroform (200 mL) and extracted with 1% HCl (100 mL), water (3 x 100 mL) and finally brine (50 mL) and then dried over anhydrous sodium sulfate. After removal of
10 the drying agent by filtration, the solution was concentrated in vacuo to give the final bis-aniline product as a gold colored oil.

Analysis of the product by ^1H NMR spectroscopy (CDCl_3) showed a complete absence of proton resonances for starting acrylate end groups
15 (5.5 – 6.4 ppm) and the presence of new signals at 6.6 and 7.1 ppm (aromatic ring; C_6H_4), 5.9 ppm (aromatic amine; $\text{H}_2\text{N}-\text{C}_6\text{H}_4$) and 3.8 ppm (methylene; $\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-$) due to the newly placed, terminal aniline moieties. FTIR spectroscopy (neat) confirmed the inclusion of primary and secondary amine groups in the product, with new resonances appearing in
20 the IR spectrum near 3442 and 3319 cm^{-1} . Additionally, size exclusion chromatography (SEC) indicated that the molecular weight of the bis-aniline product was roughly comparable to that of the butadiene di-acrylate starting material and that unwanted side reactions that might have produced higher molecular weight adducts did not take place during the
25 Michael conjugate addition process.

Example 3

The following example details the synthesis of a water soluble aniline co-monomer containing three polymerizable aniline end groups.

30



Aniline co-monomer 3

- 5 2-Aminomethyl aniline (30.1 g, 0.246 mol) dissolved in tetrahydrofuran (110 mL) was added dropwise to a solution of Sartomer SR-499 tri-
 acrylate (35.2 g, 0.247 mol reactive acrylate groups) in tetrahydrofuran (150 mL) over a 22 minute period at room temperature. After the addition
 was complete, the light tan reaction mixture was stirred under ambient
 10 conditions for a total of four days and then concentrated in vacuo to give a viscous, dark-brown oil. The crude product was warmed to 50 degrees C and then placed under high vacuum to remove traces of unreacted 2-
 aminomethyl aniline starting material by the process of sublimation. The
 final bis-aniline product isolated as a dark gold-colored oil.

15

- Analysis of the product by ^1H NMR spectroscopy (CDCl_3) showed a near
 absence of proton resonances for starting acrylate end groups (5.5 – 6.4
 ppm) and the presence of new signals near 6.6 and 7.1 ppm (aromatic
 ring; C_6H_4), 4.6 ppm (aromatic amine; $\text{H}_2\text{N}-\text{C}_6\text{H}_4$) and 3.8 ppm (methylene;
 20 $\text{C}_6\text{H}_4-\text{CH}_2-\text{NH}-$) due to the newly placed, terminal aniline moieties. FTIR
 spectroscopy (neat) confirmed the inclusion of primary and secondary
 amine groups in the product, with new resonances appearing in the IR
 spectrum near 3442 and 3319 cm^{-1} .

- 25 **Examples 4-6 describe the preparation of PANI-coated aramid pulps.**

Example 4

This example demonstrates the oxidative polymerization of aniline in the presence of an aqueous suspension of para-aramid pulp to give a PANI-coated pulp product.

Hydrated para-aramidpulp (5.0 g; 50 wt% water) was suspended in 1 N HCl (500 mL) and allowed to stir rapidly for one hour. Aniline monomer (1.00 g, 10.7 mmol) was then added to the stirred suspension. After five additional minutes, the stirred suspension was treated with a solution of ammonium persulfate initiator (2.45 g, 10.7 mmol) dissolved in water (50 mL). The resulting mixture was stirred at room temperature for 24 hours during which time the suspended pulp fibers changed color from tan to dark green-blue. The PANI coated pulp product was isolated by filtration, re-suspended in 1 N HCl (500 mL) and then rapidly stirred for 20 minutes to remove any unbound reagents or materials. The final product was isolated by a second filtration step and then dried in vacuo at 50 C for 24 h. The dried PANI-coated pulp was re-dispersible in water or in a 1N HCl solution after vigorously stirring for several minutes.

Example 5

This example demonstrates the oxidative copolymerization of a mixture of aniline and aniline co-monomer 1 in the presence of an aqueous suspension of para-aramid pulp to give a PANI-coated pulp product.

Hydrated para-aramid pulp (5.0 g; 50 wt% water) was suspended in 1 N HCl (700 mL) and allowed to stir rapidly overnight. A solution of aniline monomer (0.75 g, 8.05 mmol) dissolved into 1 N HCl (10 mL) was added to the suspension. A second solution of aniline co-monomer 1 (0.25 g, 0.545 mmol, 1.09 mmol reactive aniline groups) dissolved into 1 N HCl (10 mL) was also added to the stirred suspension. After fifteen minutes, the stirred suspension was treated with a solution of ammonium persulfate initiator (2.09 g, 9.16 mmol) dissolved in water (50 mL). The resulting mixture was stirred at room temperature for 27 hours during which time the suspended pulp fibers changed color from tan to dark green. The PANI coated pulp product was isolated by filtration, re-suspended in 1 N HCl (600 mL) and then rapidly stirred for one hour to

remove any unbound reagents or materials. The final product was isolated by a second filtration step and then dried in vacuo at 50 C for 36 h. The dried PANI-coated pulp was re-dispersible in water or in a 1N HCl solution after vigorously stirring for several minutes.

5

Example 6

This example demonstrates the oxidative copolymerization of a mixture of aniline and the organo-soluble aniline co-monomer 2 in the presence of an aqueous suspension of para-aramid pulp to give a PANI-coated pulp product.

10

Hydrated para-aramid pulp (5.0 g; 50 wt% water) was suspended in 1 N HCl (800 mL) and allowed to stir rapidly for one hour. A solution of aniline co-monomer 2 (1.00 g) dissolved into 1, 4-dioxane (20 mL) was added to the suspension in a drop-wise manner over a 15 minute period.

15

The resulting mixture was stirred for another 30 minutes to allow the aniline co-monomer 2 to evenly coat-out onto the pulp fibers. A second solution of aniline monomer (0.88 g, 9.44 mmol) dissolved into 1 N HCl (10 mL) was also added to the stirred suspension. After fifteen minutes, the stirred suspension was treated with a solution of ammonium persulfate initiator (2.45 g, 10.7 mmol) dissolved in water (15 mL). The resulting mixture was stirred at room temperature for 24 hours during which time the suspended pulp fibers changed color from tan to dark green. The PANI coated pulp product was isolated by filtration, re-suspended in 1 N HCl (500 mL) and then rapidly stirred for about one hour to remove any unbound reagents or materials. The final product was isolated by a second filtration step and then dried in vacuo at 50 C for 36 hours. The dried PANI-coated pulp was re-dispersible in water or in a 1N HCl solution after vigorously stirring for several minutes.

20

25

30

Example 7

This example compares the relative solvent stabilities of the three PANI-coated pulp products prepared in Examples 4, 5 and 6.

General Test Procedure. PANI-coated aramid pulp samples (0.10 g each) were placed into screw-capped glass vials and then treated with equivalent volumes of water, methanol, 1, 4-dioxane or N, N-dimethyl-acetamide (DMAC) (10 mL). The capped vials containing the test

5 mixtures were placed on a rotating platform and gently agitated for one hour. The contents of the vials were then allowed to settle and the relative amount of PANI removed from each of the coated pulps was qualitatively judged by examining the color of the fluid surrounding the aramid pulp

10 fibers. A clear fluid indicated that the PANI coating exhibited good solvent stability and remained bound to the pulp surface. A light green-colored fluid indicated that some of the PANI coating was removed from the pulp. A dark green solution indicated that most of the PANI coating was dissolved from the pulp fibers by the test fluid.

15

Table 1

Product from Example #	Crosslinking aniline co-monomer used	Water	Methanol	1,4-dioxane	DMAC
4	none	clear	clear	light green	dark green
5	1	clear	clear	clear	clear
6	2	clear	clear	clear	light green

The results summarized in Table 1 confirm that the use of aniline

20 co-monomers 1 and 2 in the oxidative polymerization reaction of aniline furnished PANI coated pulp products with enhanced solvent stabilities, even when tested against an aggressive solvent like DMAC. Aniline co-monomer 1 was more effective than co-monomer 2 when qualitatively evaluated in this manner.

Example 8

This example demonstrates the oxidative polymerization of aniline in a 1N HCl solution where an aqueous suspension of para-aramid pulp is added at a latter stage to give a final product that contains a mixture of PANI particles and PANI-coated pulp.

Aniline monomer (1.00 g, 10.7 mmol) and ammonium persulfate initiator (2.45 g, 10.7 mmol) were both dissolved in 1N HCl (300 mL). The resulting solution was stirred at room temperature for one hour during which time it became turbid and dark green in color. Para-aramid pulp (5.0 g; 50 wt% water) that had been pre-suspended in 1 N HCl (250 mL) was then rapidly added to the reaction mixture. The resulting heterogeneous mixture was stirred at room temperature for an additional 23 hours during which time the suspended pulp fibers changed color from tan to dark green-blue. The product was isolated by filtration, re-suspended in 1 N HCl (500 mL) and then rapidly stirred for 20 minutes to remove any residual reagents. The final product was isolated by a second filtration step and then dried in vacuo at 50 degrees C for 24 hours.

Analysis of the product mixture by Scanning Electron Microscopy (SEM) revealed the presence of small discrete particles that were randomly mixed among the larger pulp fibers. This observation was in direct contrast to an SEM analysis on the PANI coated pulp product isolated from Example 4 which showed a complete absence of particles. The dried product containing the mixture of PANI particles and PANI coated pulp was re-dispersible in water or in a 1N HCl solution after vigorously stirring for several minutes.

Example 9

This example compares electrical resistance values measured for the PANI-coated aramid pulp prepared in Example 4 to those determined for an uncoated aramid pulp control sample.

Preparation of Test Specimens: The dried PANI-coated aramid pulp product prepared in Example 4 (5.0 g) was re-suspended into 1 N HCl

(500 mL) with gentle stirring. An aliquot of this suspension (80 – 100 mL) was then slowly passed through a 30 mL glass-fritted filter funnel. After the filtration was complete, the product, now shaped into a small rounded fibrous disk, was carefully removed from the filter funnel using plastic-covered tweezers. This procedure was repeated two additional times, giving a total of three separate sample disks. The disks were dried to constant weight in an argon-purged vacuum oven set to 45 degrees C. A similar procedure was carried out for uncoated aramid pulp, giving three additional disks that would serve as controls. All of the oven dried disks prepared in this manner had diameters that ranged from 28-30 mm and thickness values that fell between 5-7 mm.

Measurement of Electrical Resistance Values: Each of the small disks prepared above was pre-treated with Flash-Dry Silver Paint (SPI Supplies, a Division of Structure Probe Inc., West Chester, PA). The paint was applied to two small (approximately 1 mm diameter) regions on the top surface of each disk. The painted regions were separated by a linear distance of 20 mm. The disks modified in this manner were dried in a vacuum oven for one hour. Two-point electrical resistance measurements were then made by carefully attaching electrical leads to the two silver-painted regions on each disk. Resistance values were determined with a standard volt-ohm multi-meter (Ideal Industries, Sycamore, IL).

The three PANI-coated pulp test specimens evaluated in this manner were electrically conductive, exhibiting electrical resistance values that ranged from 10 – 50 K ohm. In stark contrast, the uncoated aramid pulp controls were totally insulating, displaying infinitely high resistance values when evaluated in the same manner.

What is claimed is:

1. An electrically conductive pulp suitable for use as a reinforcement
5 comprising from 60 to 96 weight percent of fibers selected from the group
consisting of aromatic polyamide, aromatic copolyamide and mixtures
thereof and from 4 to 40 weight percent of conductive material coated onto
the fibers, wherein the conductive material comprises
 - (i) a polymer of aniline ,or
 - 10 (ii) a random copolymer formed from aniline and one or more
substituted aniline co-monomers that exist in the protonated
emeraldine salt form.
2. The pulp of claim 1, comprising polyaniline particles blended with
15 pulp, the pulp comprising a coating of polyaniline on the fiber surfaces.
3. The pulp of claim 1, comprising particles of a random copolymer
formed from aniline and one or more substituted aniline co-monomers
blended with pulp, the pulp comprising a coating of a random copolymer
20 formed from aniline and one or more substituted aniline co-monomers.
4. The pulp of claim 1, wherein the aromatic polyamide is para-
aramid.
5. A method of making an electrically conductive fibrous pulp suitable
25 for use as a reinforcement, the fibers being selected from the group
consisting of aromatic polyamide, aromatic copolyamide and mixtures
thereof, comprising the steps of
 - (i) forming a suspension of pulp in an aqueous acid dopant,
 - (ii) adding aniline or aniline and at least one substituted aniline co-
30 monomer to the suspension such that the weight percent ratio of the
amount of aniline, or the amount of aniline and substituted aniline co-
monomers, to the amount of pulp is in the range of from 4 to 40,

(iii) adding an initiator to the dispersion in the amount of one molar equivalent relative to aniline, or one molar equivalent relative to aniline and substituted aniline co-monomers, to effect polymerization,

(iv) stirring the pulp suspension for a sufficient time to ensure precipitation of the desired amount of aniline polymer or random copolymer onto the surface of the pulp,

(v) filtering the suspension to isolate the coated pulp product in a first filtration step,

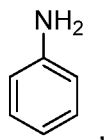
(vi) washing the coated pulp product with additional aqueous acid dopant solution, and

(vii) isolating the washed coated pulp product in a second filtration step.

6. The method of claim 5, wherein the acid dopant is selected from the group consisting of hydrochloric acid, dodecyl benzene sulfonic acid and camphorsulfonic acid.

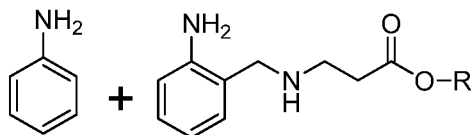
7. The method of claim 5, wherein the initiator is selected from the group consisting of ammonium persulfate, potassium persulfate and hydrogen peroxide.

8. The method of claim 5, wherein aniline is selected from the group consisting of the unsubstituted parent compound:



25

a mixture of aniline and one or more substituted aniline co-monomers:



where R contains one or more sites of unsaturation

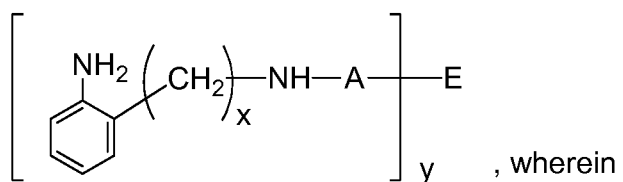
and a mixture of aniline and one or more substituted polyfunctional aniline co-monomers that can serve to crosslink the conductive polyaniline coating.

5 9. The method of claim 5, wherein the surface of the para-aramid pulp has been partially hydrolyzed prior to forming a suspension in an aqueous acid dopant.

10 10. The method of claim 5, comprising drying the coated pulp product of step (vii) under vacuum to remove water and other volatile by-products.

11. The method of claim 5, wherein the aromatic polyamide is para-aramid.

15 12. The method of claim 8, wherein the substituted polyfunctional aniline co-monomers are

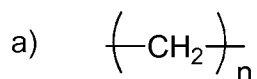


(i) x is an integer of 1 to 4,

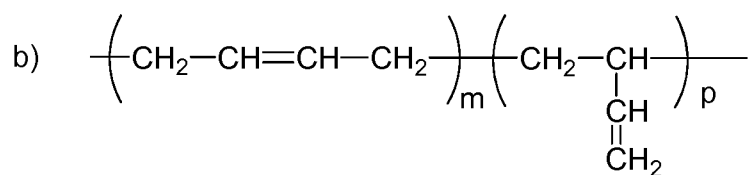
(ii) y is an integer of 2 to 4,

(iii) A is $\text{---CH}_2\text{---CH}_2\text{---}\overset{\text{O}}{\parallel}\text{C---O---}$ or $\text{---}\overset{\text{O}}{\parallel}\text{C---}$, and

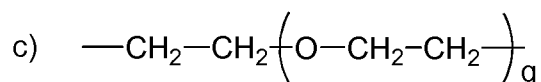
(iv) E is selected from the group consisting of:



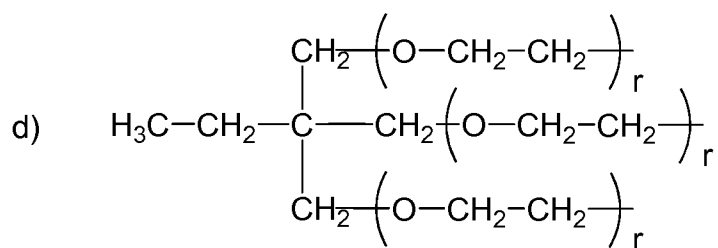
when $y = 2$ and where n is an integer from 1 to 200,



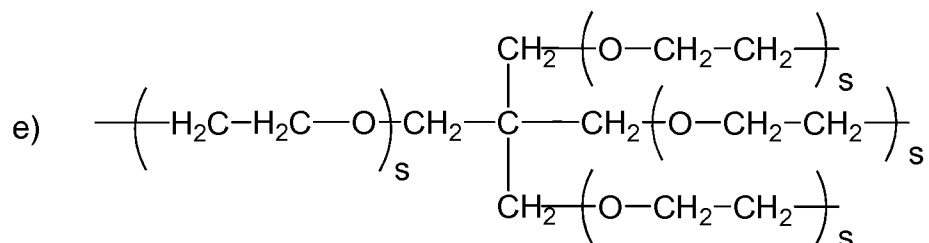
when $y = 2$ and where $m + p$ is an integer from 1 to 200,



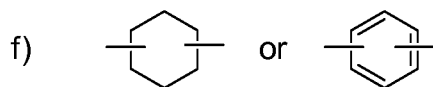
when $y = 2$ and where q is an integer from 1 to 20,



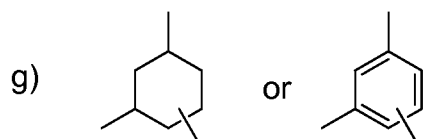
when $y = 3$ and where r is an integer from 0 to 5,



when $y = 4$ and where s is an integer from 0 to 5,



when $y = 2$, and

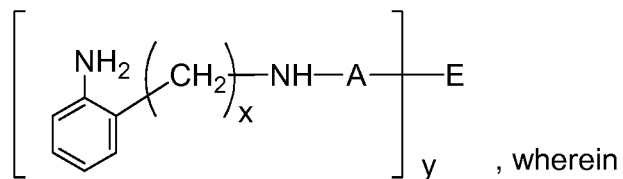


when $y = 3$.

13. The method of claim 8, wherein in an aniline co-monomer mixture,
 5 the parent aniline is used in an amount of at least 90 mol % and the substituted aniline co-monomers(s) used is in an amount of no greater than 10 mol %.

14. The method of claim 9, wherein the hydrolysis of the pulp is carried out in 10% sodium hydroxide for 1 hour to 24 hours at room temperature followed by washing to a pH of 7.

15. A substituted polyfunctional aniline co-monomer having the formula

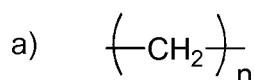


(i) x is an integer of 1 to 4,

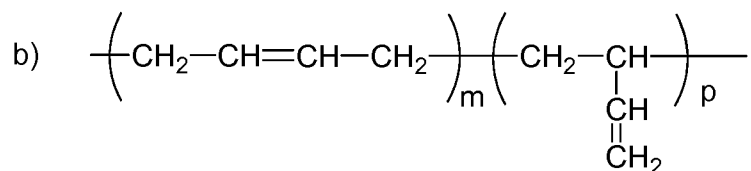
(ii) y is an integer of 2 to 4,

(iii) A is $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ or $-\overset{\text{O}}{\parallel}{\text{C}}-$, and

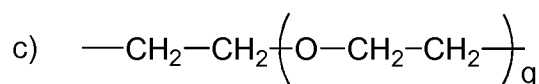
(iv) E is selected from the group consisting of:



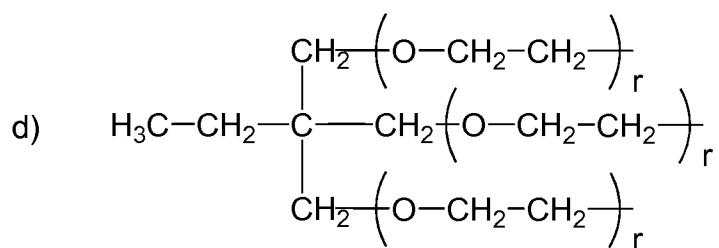
when $y = 2$ and where n is an integer from 1 to 200,



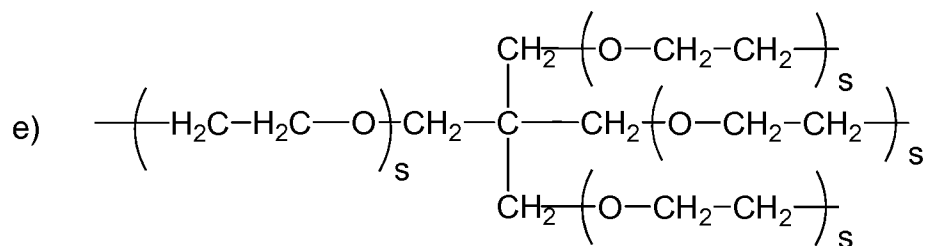
when $y = 2$ and where $m + p$ is an integer from 1 to 200,



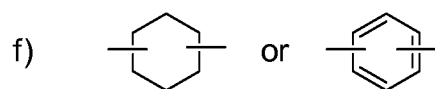
when $y = 2$ and where q is an integer from 1 to 20,



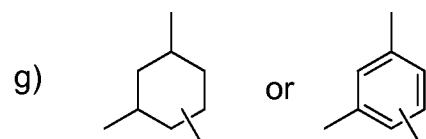
when $y = 3$ and where r is an integer from 0 to 5,



when $y = 4$ and where s is an integer from 0 to 5,



when $y = 2$, and



when $y = 3$.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011001

A. CLASSIFICATION OF SUBJECT MATTER

INV. D21H27/00 D21H13/26 D21H15/10 D21H17/49 D21H17/00
D21H21/00 D21H21/14 C08K3/00 C08K7/02 C08K9/04

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/070796 A1 (DU PONT [US]) 12 September 2002 (2002-09-12)	1,4
Y	page 2, line 8 - line 16 page 3, line 9 - line 16 claim 1	1-15
Y	----- WO 03/044250 A1 (DU PONT [US]; KELLY RENEE J [US]; FRANCES ARNOLD [US]) 30 May 2003 (2003-05-30) claims 1-22 ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

9 April 2014

Date of mailing of the international search report

17/04/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Ponsaud, Philippe

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/011001

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KIM J W ET AL: "Electroconductive fully aromatic polyamide fiber used as for, e.g. reinforcing material for electronic components, has polyaniline coated layer on outer surface of polyamide fiber", WPI / THOMSON,, vol. 2009, no. 41, 6 April 2009 (2009-04-06), XP002670719, abstract	1-15
X,P	----- WO 2013/045366 A1 (TEIJIN ARAMID BV [NL]) 4 April 2013 (2013-04-04) claims 1-10 example 5 -----	1,5

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/011001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 02070796	A1	12-09-2002	BR 0207843 A 02-03-2004
		CA 2437825 A1 12-09-2002	
		CN 1501991 A 02-06-2004	
		DE 60219146 T2 06-03-2008	
		EP 1366223 A1 03-12-2003	
		JP 4537654 B2 01-09-2010	
		JP 2004523670 A 05-08-2004	
		KR 20030084965 A 01-11-2003	
		US 6436236 B1 20-08-2002	
		WO 02070796 A1 12-09-2002	
-----	-----	-----	-----
WO 03044250	A1	30-05-2003	AT 414805 T 15-12-2008
		AU 2002363930 A1 10-06-2003	
		BR 0214232 A 21-09-2004	
		CA 2467116 A1 30-05-2003	
		CN 1585839 A 23-02-2005	
		EP 1448817 A1 25-08-2004	
		ES 2316641 T3 16-04-2009	
		JP 2005509760 A 14-04-2005	
		KR 20040066813 A 27-07-2004	
		MX PA04004642 A 13-08-2004	
		TW I238214 B 21-08-2005	
		US 2003114641 A1 19-06-2003	
		WO 03044250 A1 30-05-2003	
-----	-----	-----	-----
WO 2013045366	A1	04-04-2013	NONE
-----	-----	-----	-----