PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : F41H 5/04

A1

(11) International Publication Number: WO 93/00564

(43) International Publication Date: 7 January 1993 (07.01.93)

(21) International Application Number: PCT/US92/05018

(22) International Filing Date: 18 June 1992 (18.06.92)

(30) Priority data:
721,818 26 June 1991 (26.06.91) US

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

(72) Inventors: CHIOU, Minshon, J. ; 6618 Irongate Drive, Richmond, VA 23234 (US). YANG, Hung, Han ; 322 Harwick Drive, Richmond, VA 23236 (US).

(74) Agents: SHAFER, Robert, J. et al.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).

(81) Designated States: AU, CA, JP, KR, RU, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: p-ARAMID BALLISTIC YARN AND STRUCTURE

(57) Abstract

A laminated ballistic structure is disclosed using fabrics made from p-aramid yarn with high tenacity and elongation to break and a consequent improved ballistic performance. The ballistic structure is laminated and comprises a plurality of fabric layers made from said p-aramid yarn exhibiting an elongation to break of greater than 4.0 % a modulus of less than 600 g/d, and a tenacity of greater than 23 g/d.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland			SN	Senegal
CI	Côte d'Ivoire	KR	Republic of Korea	SU	Soviet Union
CM	Cameroon	LI	Liechtenstein	TD	Chad
CS	Czechoslovakia	LK	Sri Lanka	TG	Togo
DE	Germany	LU	Luxembourg	US	United States of America
DK	Denmark	MC	Monaco		
ES	Spain	MG	Madagascar		

Title

p-Aramid Ballistic Yarn and Structure

Background of the Invention

Field of the Invention

This invention relates to ballistic structures made using fabrics woven from p-aramid yarns having high tenacity and high elongation to break.

Description of the Prior Art

United States Patent No. 4,850,050 issued July 25, 1989 on the application of Droste et al., discloses body armor made from p-aramid yarns comprising filaments of low individual linear density. The ballistic performance of body armor made in accordance with that invention was reported to represent a 5% improvement over the comparison fabric of the prior art.

United States Patent No. 4,859,393 issued August 22, 1989 on the application of Yang and Chiou, discloses a process for making p-aramid yarns said to have a high elongation at break.

United States Patents No. 3,869,429 and 4,560,743, issued March 4, 1975 and December 24, 1985, respectively, each disclose para-aramid fibers of high quality. There is no disclosure of any specially recognized utility for fabrics from these fibers in ballistic protection.

Summary of the Invention

The present invention provides a p-aramid ballistic structure which utilizes yarns having a combination of especially high tenacity and elongation to break. The ballistic structure is laminated and comprises a plurality of fabric layers made from that p-aramid yarn exhibiting an elongation to break of greater than 4.0%, a modulus of less than 600 gpd, and a tenacity of greater than 23 gpd.

Detailed Description of the Invention

Protective garments and other ballistic materials have long been made using p-aramid fibers. P-aramid fibers are extremely strong on a weight basis and provide good ballistic protection with a relatively high

There has been great effort expended in developing yarns and fabrics with improved ballistic performance because even small improvements save the lives of users of ballistic garments. Each improvement is hard-won and highly significant. The present invention represents an improvement in ballistic performance, measured by V_{50}, of about 5%.

Poly(p-phenylene terephthalamide) fibers made by the usual processes, such as by processes described in United States Patent No. 3,869,429, exhibit yarn tenacities of greater than about 21 grams per denier, moduli of 400 to 700 grams per denier, and elongations to break of about 2.8 to 4.1%.

While strength is important to ballistic performance, strength is not the only factor which need be considered. It has now been found that the ballistic performance of fibers having a tenacity of greater than about 20 grams per denier will not be significantly improved by increase in tenacity, alone. By the same token, modulus is not now seen as an important factor in ballistic performance. Fibers with moduli greater than about 500 grams per denier will not be significantly improved in ballistic performance by increase in modulus.

Of all of the tensile properties usually tested, it has been found that the combination of tenacity and elongation to break is one of the most important parameters for ballistic performance. Yarn toughness, that is, the ability to absorb energy, is significantly affected by the combination of tenacity and elongation to break, of the fiber. While p-aramid fibers exhibit remarkable ballistic performance even at a moderate tenacity of 23 grams per denier and low elongation to break of 3.0%, the ballistic performance is rather dramatically improved with any increase in toughness.

Ballistic structures of this invention are made with yarns which are woven into fabrics; and the fabrics are formed into garments or other structures for ballistics protection. The kind of fabric or weave to which the yarn is applied is not important to realize the benefit of the invention. That is, for any fabric or weave pattern, ballistic performance obtained using the yarn of this invention will be improved over that obtained using a similar yarn having a lower toughness due to lower tenacity or lower elongation to break.

Body armor using ballistic fabrics is usually made with several layers of fabric laid or sewn together to yield a laminated structure. The laminated structure can include additional layers of other materials such as decorative or moisture resistant covering fabrics or other shock absorbing materials. The form of the laminated structure and whether or not it includes additional layers of other materials is not important to realization of the improved ballistic performance of this invention. It has been discovered that the effectiveness of any ballistic structure will be improved by utilization of yarn having relatively higher tenacity and/or elongation to break instead of similar yarn having relatively lower tenacity and/or elongation to break.

Test Methods

Ballistic Limit

Ballistic tests of the composite samples are conducted in accordance with MIL-STD-662e as follows: A lay-up to be tested is placed in a sample mount to hold the lay-up taut and perpendicular to the path of test projectiles. The projectiles are 17-grain fragment simulating projectiles (MIL-P-46593), except where indicated otherwise, and are propelled from a test barrel capable of firing the projectiles at different velocities. The first firing for each lay-up is for a projectile velocity estimated to be the likely ballistic limit (V_{50}). When the first firing yields a complete lay-up penetration, the next firing is for a projectile velocity of about 50 feet per second less in order to obtain a partial penetration of the lay-up. On the other hand, when the first firing yields no penetration or partial penetration, the next firing is for a velocity of about 50 feet per second more in order to obtain a complete penetration. After obtaining one partial and one complete projectile penetration, subsequent velocity increases or decreases of about 50 feet per second are used until enough firings are made to determine the ballistic limit (V_{50}) for that lay-up.

The ballistic limit (V_{50}) is calculated by finding the arithmetic mean of an equal number of five of the highest partial penetration impact velocities and five of the lowest complete penetration impact velocities, provided that there is not more than 125 feet per second between the highest and lowest individual impact velocities.

Tensile Properties

Tenacity is reported as breaking stress divided by linear density. Modulus is reported as the slope of the initial stress/strain curve converted to the same units as tenacity. Elongation is the percent increase in length at break. Both tenacity and modulus are first computed in g/denier units which, when multiplied by 0.8826, yield dN/tex units. Each reported measurement is the average of 10 breaks.

Tensile properties for yarns are measured at 24°C and 55% relative humidity after conditioning under the test conditions for a minimum of 14 hours. Before testing, each yarn is twisted to a 1.1 twist multiplier (for example, nominal 1500 denier yarn is twisted about 2.1 turns/inch). Each twisted specimen has a test length of 25.4 cm and is elongated 50% per minute (based on the original unstretched length) using a typical recording stress/strain device.

The twist multiplier (TM) of a yarn is defined as:

$$TM = \frac{(tpi)\ (Denier)^{1/2}}{73} = \frac{(tpc)\ (dtex)^{1/2}}{30.3}$$

Wherein tpi = turns per inch and
tpc = turns per centimeter

Tensile properties for yarns are different from and lower than tensile properties for individual filaments and such values for yarns cannot successfully and accurately be estimated from filament values.

Description of the Preferred Embodiments

EXAMPLE 1

Poly(p-phenylene terephthalamide) (PPD-T) fibers having high tenacity and high elongation were spun as described in United States Patent No. 4,340,559, using Tray G thereof. The PPD-T had an inherent viscosity of 6.3 dL/g. To make the spinning dope, the PPD-T was dissolved in 100.1% sulfuric acid to a concentration of 19.4 weight percent. The dope was deaerated under vacuum and spun through a spinneret having 672 capillaries of 2.5 mil (0.0635mm) diameter. Spinning was at a dope temperature of about 71°C directly through an air gap 0.64 cm in length and then into a spin tube together with coagulating liquid which was an aqueous solution of 8% by weight sulfuric acid maintained at 20°C. The spin stretch factor was 6.3. The coagulated yarn was forwarded to a water-washing stage, to a neutralization stage, to a drying stage on a pair of internally steam-heated rolls with surface temperature of 150°C, and then to windup on bobbins at a moisture content of about 12 weight percent. Yarn tension during washing/neutralization was 0.2 to 0.4 grams per denier (gpd) and during drying was 0.05 to 0.2 gpd. The resulting yarn was 1000 denier (1111 dtex) and 1.5 denier per filament (dpf) (1.67 dtex per filament). The yarn exhibited an elongation to break of 4.3%, a modulus of 450 gpd, and a tenacity of 24 gpd.

Test fabrics were made using the yarn of this example and control test fabrics were made using commercially-available aramid yarn sold by E. I du Pont de Nemours & Co. under the trademark designation Kevlar® 29. The control yarn exhibited an elongation to break of 3.4%, a modulus of 605 gpd, and a tenacity of 23 gpd. The control yarn was, also, 1000 denier and 1.5 denier per filament. The fabrics were plain weave with a basis weight of about 244 g/m^2 (7.1 oz/yd^2) and a construction of about 29 x 26 (W x F/inch).

Finish was removed from each of the fabrics by washing in water with detergent and rinsing in water. Thirteen layers of each of the fabrics were laid together and tested in accordance with MIL-STD-662e using the 22 caliber, 17-grain fragment simulating projectile specified in MIL-P-46593. The ballistic test result, shown in Table 1, below, was that the V_{50} for the structure of this invention was 6.4% greater than the V_{50} of the control.

TABLE 1

V_{50} (m/s)

Test	Control	This Invention
A	477.3	499.0
B	484.0	503.8
C	470.3	520.9
Average	477.2	507.9

For reasons not fully understood, the benefits of this invention are realized with non-deforming projectiles; but do not appear to extend to deformable lead bullets. Tests performed on fifteen layers of the above-described fabrics using 9 mm, full-metal jacketed lead, 124-grain NATO projectiles, yielded V_{50} of about 418 m/s with no significant difference between the fabrics.

EXAMPLE 2

For this example, PPD-T yarn was spun by the same process as was used in Example 1, above, except that the spinneret had 1000 capillaries of 2.5 mil (0.0635 mm) diameter to produce a yarn of 1500 denier (1667 dtex) and 1.5 dpf. This yarn exhibited an elongation to break of 4.8%, a modulus of 365 gpd, and a tenacity of 23.3 gpd.

Fabrics, again, were made using the yarn of this example and control test fabrics were made using commercially-available aramid yarn sold by E. I du Pont de Nemours & Co. under the trademark designation Kevlar® 29. The control yarn exhibited an elongation to break of 3.6%, a modulus of 560 gpd, and a tenacity of 23 gpd. The control yarn was, also, 1500 denier and 1.5 denier per filament. The fabrics were plain weave with a basis weight of about 325 g/m^2 (9.6oz/yd^2) and a construction of about 24 x 24 (W x F/inch).

Finish was removed from each of the fabrics by washing in water with detergent and rinsing in water. Ten layers of each of the fabrics were laid together and tested in accordance with MIL-STD-662e using the 22 caliber, 17-grain fragments imulating projectile specified in MIL-P-46593. The ballistics test result, shown in Table 2, below, was that the V_{50} for the structure of this invention was 4.1% greater than the V_{50} of the control.

TABLE 2

V_{50} (m/s)

Test	Control	This Invention
A	442.3	480.4
B	449.6	456.9
C	450.2	460.2
Average	447.4	465.8

Tests performed on twelve layers of the above-described fabrics using 9 mm, full-metal jacketed lead, 124-grain NATO projectiles, yielded V50 of 395 m/s with no significant difference between the fabrics.

EXAMPLE 3

Poly(p-phenylene terephthalamide) (PPD-T) fibers having high tenacity and high elongation were spun as described in United States Patent Application Serial No. 07/673,552, filed March 8, 1991. The PPD-T had an inherent viscosity of 6.3 dL/g. To make the spinning dope, the PPD-T was dissolved in 100.1% sulfuric acid to a concentration of 19.4 weight percent. The dope was deaerated under vacuum and spun through a multiple-orifice spinneret having capillaries of 2.0 mil (0.051mm) diameter. Spinning was at a dope temperature of about 71°C directly through an air gap 0.64 cm in length and then into a spin tube together with coagulating liquid which was an aqueous solution of 8% by weight sulfuric acid maintained at 2°C. The spin stretch factor was 4.14. The coagulated yarn was forwarded to a water-washing stage, to a neutralization stage, to a drying stage on a pair of internally steam-heated rolls with surface temperature of 125°C, and then to windup on bobbins at a moisture content of about 12 weight percent. Yarn tension during washing/neutralization was 0.2 to 0.3 grams per denier (gpd) and during drying was 0.2 to 0.3 gpd. The resulting yarn was 1500 denier (1667 dtex) and 1.5 denier per filament (dpf)(1.67 dtex per filament). It exhibited an elongation to break of 4.2%, a modulus of 510 gpd, and a tenacity of 26.2 gpd.

Test fabrics were made using the yarn of this example and control test fabrics were made using commercially-available aramid yarn sold by E. I du Pont de Nemours & Co. under the trademark designation Kevlar® 29. The control yarn exhibited an elongation to break of 3.4%, a modulus of 605 gpd, and a tenacity of 23 gpd. The control yarn was, also, 1500 denier and 1.5 denier per filament. Two fabrics were woven: one was a plain weave with a basis weight of about 339 g/m^2 (10.0 oz/yd^2) and a construction of about 24 x 24 (W x F/inch); and the other was a 2x2 basket weave with a basis weight of about 474 g/m^2 (14.0 oz/yd^2) and a construction of about 36 x 35.

Finish was removed from each of the fabrics by washing in water with detergent and rinsing in water. Twelve layers of each of the basket weave and 17 layers of each of the plain weave fabrics were laid together and tested in accordance with MIL-STD-662e using the 22 caliber, 17-grain fragment simulating projectile specified in MIL-P-46593. The ballistic test result, shown in Table 3, below, was that the V_{50} for the structure of this invention was 7.4% greater than the V_{50} of the control for the basket weave fabric construction and 3.0% greater than the V_{50} of the control for the plain weave fabric construction.

TABLE 3

V_{50} (m/s)

	Basket Weave		Plain Weave	
Test	Control	This Invention	Control	This Invention
A	532.2	558.4	559.0	---
B	507.2	555.7	560.5	567.8
C	520.6	562.4	555.0	581.3
Average	520.0	558.7	558.0	574.6
Improvement	--	+7.4%	--	+3.0%

In a second experiment, using the same yarn as was previously used in this example, a second test fabric was woven having a 2X2 basket weave with a basis weight of about 494 g/m^2 (14.6 oz/yd^2) and a construction of 35X35. The ballistic test was conducted in the same way and the V_{50} for this test was found to be 539.6 m/s compared with 501.5 m/s for the control fabaric. The ballistic structure of this invention, thus, yielded a V_{50} which was 7.6% greater than that of the control.

EXAMPLE 4

Using the same yarn as was used in Example 2, a test fabric was woven the same as that used in Example 3. The ballistic test resulted in V_{50}, for the test fabric, of 548.2 m/s and V_{50}, for the control fabric, of 520.0 -- an improvement of 5.4%.

Claims

1. A laminated ballistic structure comprising a plurality of fabric layers made from p-aramid yarns exhibiting an elongation to break of greater than 4.0%, a modulus of less than 600 gpd, and a tenacity of greater than 23 gpd.

2. The laminated ballistic structure of Claim 1 wherein there are additional layers of other materials included in the structure.

3. The laminated ballistic structure of Claim 1 wherein the p-aramid is poly(p-phenylene terephthalamide).

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/05018

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 F41H5/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	F41H ; D01F

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]
X	WOLSKY S.P CZANDERNA A.W. 'Methods and phenomena vol. 5. Ballistic materials and penetration mechanics' 1980 , ELSEVIER SCIENTIFIC PUBL. CIE. , AMSTERDAM see page 81 - page 86; table 1	1,3
Y		2

Y	WO,A,9 006 389 (ALLIED SIGNAL INC) 14 June 1990 see page 11, line 10 - page 12, line 26	2
A		1,3

A	US,A,4 560 743 (FUJIWARA ET AL) 24 December 1985 cited in the application see column 1, line 8 - line 12 TABLE 1, EXAMPLES 1-1 - 1-6	1-3

	-/--	

° Special categories of cited documents : [10]

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

"E" earlier document 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

"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

1 **IV. CERTIFICATION**

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
06 NOVEMBER 1992	24. 11. 92
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	DOUSKAS 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.
A	US,A,4 859 393 (YANG ET AL) 22 August 1989 cited in the application Table, eaxmples 1-A & 1-E	1-3
A	US,A,3 869 429 (BLADES) 4 March 1975 cited in the application TABLE II, EXAMPLE I	1-3
A	WO,A,8 703 674 (ALLIED CORPORATION) 18 June 1987 see page 6, line 1 - page 8, line 8; claim 45	1-3

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 9205018 SA 61384

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 06/11/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9006389	14-06-90	US-A-	5093158	03-03-92
		CA-A-	2003790	28-05-90
US-A-4560743	24-12-85	JP-A-	60052617	25-03-85
		DE-A-	3467193	10-12-87
		EP-A,B	0138011	24-04-85
US-A-4859393	22-08-89	AU-A-	3087189	07-09-89
		EP-A-	0331156	06-09-89
		JP-A-	1280014	10-11-89
		US-A-	4902774	20-02-90
US-A-3869429	04-03-75	AU-B-	474823	05-08-76
		AU-A-	4153572	01-11-73
		BE-A-	782795	30-10-72
		CA-A-	996716	14-09-76
		CH-A-	531057	30-11-72
		DE-A,B,C	2219703	09-11-72
		DE-C-	2265806	07-03-91
		DE-C-	2265807	10-05-90
		FR-A,B	2134582	08-12-72
		GB-A-	1393011	07-05-75
		JP-C-	1370949	25-03-87
		JP-A-	51030257	15-03-76
		JP-B-	59014567	05-04-84
		JP-A-	51023566	25-02-76
		JP-B-	59014568	05-04-84
		LU-A-	65248	13-07-72
		SE-B-	381684	15-12-75
WO-A-8703674	18-06-87	US-A-	4681792	21-07-87
		CA-A-	1263267	28-11-89
		EP-A-	0287561	26-10-88
		JP-T-	63502769	13-10-88

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82