(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
15 May 2003 (15.05.2003)

PCT

(10) International Publication Number
WO 03/040454 A1

(51) International Patent Classification[7]: D04H 3/00, D01F 8/14

(21) International Application Number: PCT/EP02/12479

(22) International Filing Date:
6 November 2002 (06.11.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/332,883 6 November 2001 (06.11.2001) US

(71) Applicant: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.** [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors: **CARSON, Ian, Guilland**; Avenue Jean Monnet 1, Louvain-la-Neuve, B-1348 Ottignies (BE). **HWO, Charles, Chiu-Hsiung**; 2710 Sugar Land Drive, Sugar Land, TX 77478 (US). **SUN, Christine, Qin**; 1321 White Avenue, 216 Tandec Building, Knoxville, Tennessee 37996 (US). **ZHANG, Dong**; 1321 White Avenue, 217 Tandec Building, Knoxville, TN 37996 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/040454 A1

(54) Title: POLY(TRIMETHYLENE TEREPHTHALATE) BASED SPUNBONDED NONWOVENS

(57) Abstract: This invention is a spubonded nonwoven material which is formed of polytrimethylene terephthalate (PTT). This material may be a microfiber material which is 1 dpf or less in fiber diameter. This nonwoven material is unique in that it has a hydrostatic head of no more than 10 cm, preferably no more than 5 cm.

POLY(TRIMETHYLENE TEREPHTHALATE) BASED SPUNBONDED NONWOVENS

Field of the Invention

This invention relates to spunbonded microfiber nonwoven materials made from polytrimethylene terephthalate.

Background of the Invention

Thermoplastic resins have been extruded to form fibers and webs for a number of years. The most common thermoplastics for this application are polyolefins and polyesters. Other materials such as polyetheresters, polyamides and polyurethanes are also used for this purpose. Each material has its characteristic advantages and disadvantages vis-a-vis the properties desired in the final product to be made from such fibers.

In nonwovens industries, fibers have been developed for use in meltblown and spunbond processes to make nonwovens webs. Dupont developed the first commercial spunbond process in the late 1950's. A primary factor in the production of spunbond fabrics is control of four simultaneous integrated operations: filament extrusion, drawing, laydown, and bonding. In its simplest form, a spunbond line consists of the following elements: an extruder for forming filaments; a metering pump; a die assembly; a filament spinning, drawing, and deposition system; a belt for collecting the filaments; a bonding zone; and a winding unit. There are three basic bonding techniques employed in a spunbond process: thermal, adhesive/chemical, and needling. In the former two, point and area bonding are used using heat and pressure to bond in point bonding and usually only heat in area

bonding. These are well known and commonly used techniques in the industry.

The term "bicomponent" usually refers to fibers which have been formed at least two polymers extruded from separate extruders but spun together to form one fiber. The configuration of such a bicomponent fiber may be a sheath/core arrangement wherein one polymer is surrounded by another or may be a side by side arrangement. It was often desirable that the fabics have the combination of the advantages of different polymers in one spun fiber.

Summary of the Invention

This invention is a spunbonded nonwoven material which is formed of polytrimethylene terephthalate (PTT). This material may be a microfiber material which is 1 dpf (denier per filament) or less in fiber diameter. This nonwoven material is unique in that it has a hydrostatic head of no more than 10 cm, preferably no more than 5 cm. Preferably, the liquid strike-through is no more than 25 seconds, more preferably no more than 15 seconds, even more preferably no more than 10 seconds, and most preferably no more than 7 seconds, and thus it is better than that of PET. Thus, the PTT nonwoven web is useful as a stocking for a diaper since it is important that materials for this use have low liquid strike-through time. It is preferable that the web also has good permeability to air. Preferably, the air permeability is at least 200 $m^3/m^2/min$.

This invention also includes bicomponent spunbonded microfiber nonwoven materials made from PTT wherein at least two different polymers have been extruded and spun together in either a side by side or core/sheath configuration and wherein at least one of the polymers is polytrimethylene terephthalate (PTT). The ratio of PTT

to the other polymer(s) ranges from 1:99 to 99:1, based on the weight of the polymers. The preferred weight ratio range of PTT to other polymer(s) is 25:75 to 75:25 and the most preferred ratio is 25:75 to 50:50. The other polymer(s) in PTT based spunbonded nonwoven may be one of the following thermoplastics: polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyamide (PA), and polylactide (PLA).

The present invention also provides a process for making such a bicomponent fiber. The present invention also provides a process for making such a spunbonded microfiber nonwoven material.

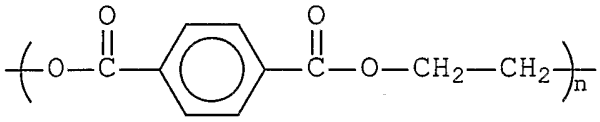
Detailed Description of the Invention

Spunbonding is a process to make microfiber nonwovens from thermoplastic polymers wherein the melt filaments are first formed by extrusion and drawing and then are laid on a continuous belt. Bonding is then accomplished by several methods such as hot roll calendaring or by passing the web through a saturated steam chamber at an elevated pressure. It has become an important industrial technique in nonwovens because of its ability to produce fabrics of microfiber structure suitable for filtration media, thermal insulators, battery separators, oil absorbents and many laminate applications. Polypropylene (PP) is the most widely used polymer for this process. Others such as polyethylene (PE), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyamide (PA) can be also used to produce the spunbonded webs. A lot of efforts have been made in the last 30 years on the process study, new resin and product development, and process improvement.

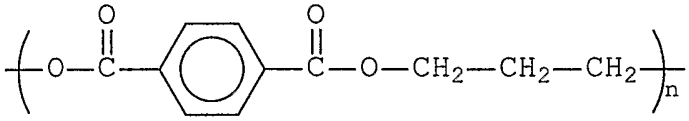
Polytrimethylene terephthalate (PTT) is primarily a linear aromatic polyester which can be prepared from the condensation polymerization of 1,3-propane diol and terephthalic acid. For commercial applications, it is desirable to produce PTT having an intrinsic viscosity greater than 0.7 dl/g and preferably greater than 0.8 dl/g. PTT itself is described more specifically and processes for making it also in U.S. Patent 6,277,947, which is herein incorporated by reference.

PTT, a member of the polyester family, is based upon a three-carbon diol. Its structure is shown below along with those of PET and PBT which are based on two-carbon and four-carbon diols, respectively.

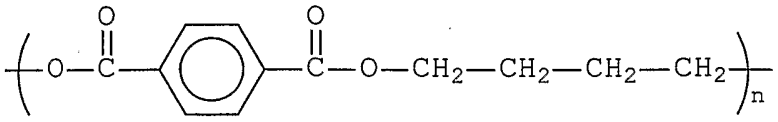
PET



PTT



PBT



PTT combines the physical properties of PET (strength, toughness, stiffness, heat resistance) with the processing advantages of PBT (low melt and processing temperatures, rapid crystallization, faster production cycles). PTT is less rigid than PET, exhibiting greater elasticity. Other desirable properties of PTT are resilience, softness, elastic recovery, moisture resistance, chemical resistance, dimensional stability,

stain resistance, weather/UV resistance and ease of dying or painting into many different colors. PTT does very well in the carpet industry, textiles, films and other thermoplastic applications.

Many polymers can be used in this invention as the other polymer fiber in a bicomponent structure but polypropylene is preferred. The polypropylene which can be used in the present invention is commercially available crystalline isotactic polypropylene. These products are well known and have been the subject of many patents, including U.S. Patents 3,112,300 and 3,112,301, which are herein incorporated by reference. Isotactic polypropylene is a straight chain of propylene units wherein the methyl groups are all aligned on one side of the polymer chain.

The bicomponent spunbonded microfiber nonwoven material which is comprised of at least two different polymers may be made by extruding and spinning them together in a core/sheath configuration. The bicomponent fiber material may be made by a process which comprises extruding at least two different polymers and spinning them together in a side by side configuration.

EXAMPLES

The PTT samples of nonwovens used herein were produced in a Reifenhauser spunbond line. The polyethylene terethphalate (PET) and polypropylene (PP) samples were commercially available materials.

Like PET and PBT, PTT absorbs moisture which causes thermal degradation of PTT at melt processing temperatures. Drying of the polymer is required before spunbonding and the MFR measurement. The drying condition was: 120 °C for 3 hours, which reduced moisture

content from 0.22% before drying to 0.003% (30 ppm) after drying. The MFR value of PTT was 385 (tested at 270 °C) and 844 (tested at 300 °C) indicating that a melt temperature of 270-300 °C is suitable for the spunbonded process.

Test and Characterization

Testing of these webs included basis weight (g/cm^2), fiber diameter (um), air permeability (ASTM D 737 - $m^3/m^2/min$), liquid strike-through (seconds), and hydrostatic head (IST 80.4-92 - cm). The fiber diameter was measured by optical microscope with the software of Image Pro. Liquid strike-through is measured by using a Lenzing Lister strike-through tester.

Results

The PTT spunbonded nonwovens sample had a basis weight of 20.26 and a fiber diameter of 14.99. The PET spunbonded nonwovens sample had a basis weight of 22.68 and a fiber diameter of 10.81. The PP spunbonded nonwovens sample had a basis weight of 20.63 and a fiber diameter of 12.24. The basis weight and fiber diameters of these samples are relatively close for comparative purposes.

The air permeability of the PTT, PET, and PP nonwovens webs was 240, 135, and 129 $m^3/m^2/min$, respectively. The liquid strike-through for the three samples was 7.24, 27.12, and >1000 seconds, respectively, and the hydrostatic head was 5.7, 5.7, and 16.5 cm, respectively. It can be seen that the PTT web exhibits the best combination of hydrostatic pressure and liquid strike-through (both low) of the three webs and is thus the most suitable for use in filtration applications.

C L A I M S

1. A spunbonded nonwoven material with a hydrostatic head of no more than 10 cm which is comprised of polytrimethylene terephthalate.

2. The material of claim 1 wherein the hydrostatic head is no more than 5 cm.

3. The material of claim 1 wherein the liquid strike-through is no more than 25 seconds.

4. The material of claim 3 wherein wherein the liquid strike-through is no more than 15 seconds.

5. The material of claim 4 wherein the liquid strike-through is no more than is 10 seconds.

6. The material of claim 5 wherein the liquid strike-through is no more than 7 seconds.

7. The material of claim 1 wherein the web is a bicomponent web which is comprised of at least two different polymers and the other polymer(s) is (are) selected from the group consisting of polypropylene (PP), polyethylene (PE), polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyamide (PA), and polylactide (PLA).

8. The bicomponent spunbonded nonwoven material of claim 7 wherein the polymers have been extruded and spun together in a core/sheath configuration.

9. The bicomponent spunbonded nonwoven material of claim 7 wherein the polymers have been extruded and spun together in a side by side configuration.

INTERNATIONAL SEARCH REPORT

In onal Application No
PCT/EP 02/12479

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D04H3/00 D01F8/14

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)
IPC 7 D04H D01F

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 practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 28122 A (HAGGARD JEFFREY S ;HILLS INC (US); HARRIS W SCOTT (US); HILLS WILL) 10 June 1999 (1999-06-10) page 11, line 10 - line 21; claims 5,6,29 ---	1-9
X	US 6 139 954 A (MCCONNELL RICHARD L ET AL) 31 October 2000 (2000-10-31) column 12, line 8 - line 31; claim 23 ---	1-9
X	WO 00 73552 A (FOSS MFG CO INC) 7 December 2000 (2000-12-07) page 6, line 12 - line 17 ---	1-9
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in 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 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 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	Date of mailing of the international search report
24 February 2003	27/03/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Mangin, S

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Int onal Application No
PCT/EP 02/12479

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 09, 30 July 1999 (1999-07-30) & JP 11 107154 A (ASAHI CHEM IND CO LTD), 20 April 1999 (1999-04-20) abstract -----	1-9

INTERNATIONAL SEARCH REPORT

Ir nal Application No
PCT/EP 02/12479

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9928122 A	10-06-1999	AU 1802499 A	16-06-1999
		WO 9928122 A1	10-06-1999
		US 6471910 B1	29-10-2002
US 6139954 A	31-10-2000	US 6197856 B1	06-03-2001
		US 6132868 A	17-10-2000
		BR 9913205 A	22-05-2001
		BR 9913206 A	22-05-2001
		CN 1330735 T	09-01-2002
		CN 1324415 T	28-11-2001
		EP 1108075 A1	20-06-2001
		EP 1115925 A1	18-07-2001
		JP 2002523646 T	30-07-2002
		JP 2002523647 T	30-07-2002
		WO 0012791 A1	09-03-2000
		WO 0012792 A1	09-03-2000
		US 6231976 B1	15-05-2001
		CA 2301522 A1	04-03-1999
		CN 1277641 T	20-12-2000
		EP 1015674 A1	05-07-2000
		JP 2001514336 T	11-09-2001
		WO 9910573 A1	04-03-1999
		CA 2308627 A1	20-05-1999
		CN 1285881 T	28-02-2001
		EP 1029120 A1	23-08-2000
		JP 2001522947 T	20-11-2001
		WO 9924648 A1	20-05-1999
WO 0073552 A	07-12-2000	AU 5162800 A	18-12-2000
		EP 1212478 A1	12-06-2002
		WO 0073552 A1	07-12-2000
JP 11107154 A	20-04-1999	NONE	