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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 December 2005 (08.12.2005)

PCT

(10) International Publication Number
WO 2005/116118 A1

(51) International Patent Classification[7]: C08J 5/18, C08L 67/02, A61L 15/22, C08L 3/00

(21) International Application Number: PCT/EP2005/005495

(22) International Filing Date: 20 May 2005 (20.05.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
MI2004A001039 25 May 2004 (25.05.2004) IT

(71) Applicant (*for all designated States except US*): **NOVAMONT S.P.A.** [IT/IT]; Via G. Fauser, 8, I-28100 Novara (IT).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): **DEL TREDICI, Gianfranco** [IT/IT]; Via Sempione, 31, I-21018 Sesto Calende (VA) (IT).

(74) Agents: **ZANOLI, Enrico** et al.; Zanoli & Giavarini S.r.l., Viale Bianca Maria, 35, I-20122 Milano (IT).

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

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

Declaration under Rule 4.17:
— *of inventorship (Rule 4.17(iv)) for US only*

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 2005/116118 A1

(54) **Title:** PERFORATED BIODEGRADABLE FILMS AND SANITARY PRODUCTS OBTAINED THEREFROM

(57) **Abstract:** Described herein is a perforated biodegradable film produced from mixtures containing at least one aliphatic or aliphatic-aromatic biodegradable polymer, from dicarboxylic acid or hydroxy acid, and from a diol in a mixture with at least one polysaccharide derivative, preferably maize starch.

PERFORATED BIODEGRADABLE FILMS AND SANITARY PRODUCTS OBTAINED THEREFROM

DESCRIPTION

The present invention relates to perforated biodegradable films and to sanitary products obtained from said films, in particular topsheets for sanitary articles for women.

The films used as internal films in contact with the skin (referred to as topsheets) for sanitary articles for women are currently for the most part produced with synthetic materials, typically polyethylene or non-woven fabric made of polypropylene or polyethylene coupled to non-woven fabric. Consequently, they are products of a completely synthetic origin and may therefore constitute a possible source of low compatibility with the skin with which they come into contact.

A drawback of a more general nature linked to the use of current materials depends upon their origin from non-renewable sources.

A further drawback is their high environmental impact since they cannot be disposed of along with the fraction of waste to be sent on for composting but must be disposed of in dumps or by incineration.

The aforementioned drawbacks are overcome by the perforated biodegradable film according to the present invention, which proves particularly suited for being used as topsheet for sanitary articles for women.

The perforated film according to the present invention can however be conveniently used for further applications also in fields different from the sanitary field.

By way of non-limiting example, it may be mentioned the use of the film as absorbent material for packaging foodstuffs, such as meat and fish, which may present leakage of liquid.

The perforated biodegradable film according to the invention has a greater biocompatibility than traditional plastic materials. The film according to the invention moreover exhibits mechanical and functional properties comparable with those of plastic films of synthetic origin. In particular, the film has an excellent wetback property (i.e., the capacity for the perforated film not to allow fluids to flow back even under pressure to the area of the body from which they come) and an excellent strike-through time (i.e., the time required for a liquid to pass through the film), which render it particularly suited for receiving body fluids.

Finally, the perforated film exhibits excellent characteristics of flexibility, i.e., it is readily conformable to the body surfaces and responds promptly to the external forces of deformation.

In particular, the present invention is aimed at a film produced from a composition containing at least one aliphatic or aliphatic-aromatic biodegradable polymer, from dicarboxylic acid or hydroxy acid, and from a diol in a mixture with at least one polysaccharide derivative.

Examples of diacids are succinic acid, oxalic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, undecanoic acid, dodecanoic acid, azelaic acid, sebacic acid, and brassilic acid. Particularly preferred are azelaic acid, sebacic acid, and brassilic acid or mixtures thereof.

Specific glycols are ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, 1,2- and 1,3-propylene glycol, dipropylene glycol, 1,3-butane diol, 1,4-butane diol, 3-methyl-1,5-pentane diol, 1,6-hexane diol, 1,9-nonane diol, 1,11-undecane diol, 1,13-tridecane diol, neopentyl glycol, polytetramethylene glycol, 1,4-cyclohexane dimethanol and cyclohexane diol. These compounds can be used alone or in mixtures. Particularly preferred are ethylene glycol, diethylene glycol and 1,4-butane diol.

Typical hydroxy acids include glycolic acid, lactic acid, 3-hydroxybutyric acid, 4-hydroxybutyric acid, 3-hydroxyvaleric acid, 4-hydroxyvaleric acid, 6-hydroxycaproic acid, and further include cyclic esters of hydroxycarboxylic acids, such as glycolide, dimers of glycolic acid, ϵ-caprolactone and 6-hydroxycaproic acid.

As regards the aromatic part, the biodegradable polymer used in the perforated film according to the present invention preferably contains a polyfunctional aromatic compound such as, for example, a phthalic acid, in particular terephthalic acid, bisphenol A, hydroquinone, and the like. Terephthalic acid is particularly preferred.

Particularly preferred are polymers with an aromatic part constituted by terephthalic acid and an aliphatic part constituted by diacid diols, and/or hydroxy acids, with C_2-C_{20} aliphatic chain, whether branched or otherwise (possibly with a chain extended with isocyanates, anhydrides or epoxides) and in particular polyesters with a base of terephthalic acid, adipic acid or sebacic acid and butane diol. Examples of this type of materials are the product sold with the trade name Ecoflex by BASF AG or the product sold with the trade name Eastarbio by Eastman Chemical.

The biodegradable polyesters used for the production of the film according to the invention can be polymerized via polycondensation or, as in the case of glycolide and of lactones, by ring opening, as is known in the literature. In addition, the polyesters can be polymers branched through the introduction of polyfunctional monomers such as glycerine, epoxidized soya oil, trimethylol propane and the like or polycarboxylic acids such as butantetracarboxylic acid. Furthermore, the polyesters may also be modified with chain extensors such as difunctional, trifunctional or tetrafunctional anhydrides, such as maleic anhydride, trimellitic anhydride and pyromellitic anhydride, with polyepoxides, or with aliphatic and aromatic isocyanates.

Regrading with isocyanate can occur in the molten state, either at the end of the reaction of polymerization or in the step of extrusion, or in the solid state.

In order to improve the characteristics of filmability, there may be added amides of aliphatic acids, such as oleamide, stearamide, erucamide, behenamide, N-oleylpalmitamide, N-stearylerucamide and other amides, salts of fatty acids, such as aluminium stearate, zinc stearate or calcium stearate, and the like. The amounts of these additives may vary from 0.05 to 7 parts and preferably between 0.1 and 5 parts on the mixture of polymers.

The polysaccharide used for preparation of the mixture for the production of the film according to the present invention can be a native starch, such as preferably starches from maize, potatoes, tapioca, rice, wheat, peas and even a starch with high contents of amylose, and the so-called waxy starches. Physically and/or chemically modified starches can also be used, including ethoxylated starches, oxypropylated starches, acetated starches, butyrated starches, propinated starches, cationic starches, oxidized starches, reticulated starches, gelatinized starches, destructured starches and starches complexated by polymeric structures. Destructurized native maize starch is particularly preferred.

Conveniently, the mixture for the production of the film according to the invention can contain one or more plasticizers. The plasticizers that can be used are, for example, the ones described in the patent EP-0 575 349, the content of which is incorporated in the present invention. Particularly suitable are glycerine, sorbitol, mannitol, erythritol, polyvinyl alcohol with low molecular weight, in addition to the oxyethylated and oxypropylated derivatives of the aforesaid compounds, citrates and acetines.

The starting compositions can moreover contain suitable additives, such as lubricating agents or dispersing agents, colouring agents, fillers, surfactants, etc.

With reference to the surfactants, non ionic surfactants, such as low molecular PEG, are preferred. They can be directly incorporated in the composition or coated on the film according to the invention.

The starting compositions for the production of the film according to the invention can be fed directly to the extruder or else can be fed in the form of pre-formed granules.

Perforated films are already used in pantie liners; in particular, wide use is made of plastic films perforated in vacuum conditions with funnel-shaped holes. As regards the technology of production, there exist different methods of perforation, such as for example:

(1) hot etching;

(2) calendering by friction between two cylinders one of which is engraved and the other smooth;

(3) cutting and extension perpendicular to the cut;

(4) use of male-female cylinders;

(5) hot-needle method; and

(6) use of jets of water on a mesh support or on a perforated drum to guarantee formation of through holes.

For the perforated biodegradable films according to the invention hot perforation in vacuum conditions with production of conical holes is particularly preferred. Particularly advantageous is the use of holes with different shapes thus allowing to increase the resistance to the elastic return of the film. Particularly preferred are perforated biodegradable films with an open area (i.e. the overall area of the holes) of between 5% and 75%, preferably between 10% and 65%, and still more preferably between 15% and 55%, with a hole density between 10 and 200 holes/cm^2, preferably between 30 and 150 holes/cm^2 and still more preferably between 50 and 120 holes/cm^2.

The biodegradable perforated film according to the present invention can be advantageously used also for providing a completely biodegradable sanitary article when associated to other components made of biodegradable material.

In particular, the biodegradable perforated film according to the present invention can be advantageously combined with a biodegradable film used as backsheet (i.e., the film set on the outer surface of the hygiene article with containment functions) for sanitary articles. In a particularly advantageous way, said backsheet is constituted by a biodegradable film having a starch-based composition.

An important function that must be performed by the film used as backsheet in sanitary products such as disposable nappies or pantie liners is that of biological barrier, i.e., the property of the film to block passage of possible pathogenic agents from the part in contact with the body towards the outer environment, and viceversa. Another important property of the film used as backsheet in sanitary products is breathability, i.e., the ability of the film to be impermeable to liquids and permeable to vapours.

Currently, the breathable film set on the outer surface (backsheet) of most sanitary products is made of microperforated polyethylene. The breathable film made of polyethylene is provided with microholes that increase the permeability to water vapour considerably, thus facilitating transpiration. However, the presence of the microholes represents a limit to the actual barrier that the film can exert. The backsheet in fact is not capable of blocking passage of possible pathogenic agents present in the faeces outwards, i.e., it is not able to act as a complete biological barrier.

The possibility of a contamination of the backsheet caused by agents present in the faeces may have severe consequences from the hygienic-sanitary standpoint, especially in communities where there are small children (nurseries, infant schools, hospitals, etc.).

Starch-based biodegradable materials are characterized by high values of permeability to water vapour. Such values are sufficiently high to enable their use as backsheet films. Said permeability is not due to the presence of microholes in the structure of the film, but to the starch, which has a high permeability to water vapour. Tests carried out according to the ASTM F 1671-97b standard on films made of Mater-Bi® NF01U, a material produced by Novamont SpA, have shown that said films act as a complete biological barrier. The same tests carried out on microperforated polyethylene indicate that this material enables passage of viruses from one side of the film to the other. Consequently, microperforated polyethylene affords advantages from the standpoint of comfort, but proves inadequate from the sanitary standpoint.

Finally, the perforated biodegradable film according to the invention exhibits excellent processability and a complete compatibility with the new types of non-woven fabric.

<u>EXAMPLE 1</u>

A film made with a composition with a base of starch and aliphatic aromatic polyester commercially available from Novamont SpA under the trademark Mater-Bi® NF866, was fed into a machine for hot embossing in vacuum conditions with funnel-shaped holes to obtain a film having a substance (mass per unit area) of approximately 25 g/m^2 and conical perforations. The density of the holes was approximately 100 $holes/cm^2$.

Said film was then tested to evaluate the level of cytotoxicity thereof as well as the mechanical and functional properties.

<u>Cytotoxicity test</u>

A film having a composition according to the invention but without perforations was compared with a film of polyethylene coupled to non-woven fabric commonly used as backsheet in hygiene articles. The films were analysed according to the methods listed below.

1) Quantitative assessment of the cell growth by means of measurement of the number of dead cells via counting in a Burker chamber.
2) Highlighting of any possible morphological alterations, such as, alteration of the cell "spreading" (flattened shape), presence of vacuoles (universally considered as a symptom of cellular suffering), and presence of granules released by the cells in the culture medium.
3) Evaluation of cell vitality by means of the method of exclusion of Trypan Blue (vital stain) and control at the optical microscope in phase contrast.

The tests were carried out on a cell line of keratinocytes (HaCat), i.e. epidermal cells that constitute the outermost skin layer. The cells were spread in 6-well dishes and cultured in complete DMEM medium in bovine foetal serum and antibiotics in a thermostatted environment at 37°C in an atmosphere of CO_2 at 95% and O_2 at 5%. The experiments were conducted starting from a total of 500,000 cells per specimen and setting them in contact with 1 cm^2 of film reduced into 10 fragments of equal dimensions.

Cells in a culture without the addition of film were used as control. The qualitative and quantitative evaluations were made after 24 hours of incubation. Six experiments were carried out.

The results of the test are listed hereinafter.

1) The cell growth was significantly greater in the presence of the Mater-Bi NF866 film as compared to the case where the film of coupled polyethylene was used, whilst the difference between the case where the NF866 film was used and the control was not significant, this confirming that the Mater-Bi NF866 film does not have a cytotoxic activity.

   The cells in contact with the film made of coupled polyethylene had a growth significantly smaller than that of the cells treated with the Mater-Bi NF866 film and than that of the control.
2) Evaluation of the morphology did not reveal any cell alteration.

The perforated biodegradable films according to the present invention consequently show characteristics of non-cytotoxicity, which highlight the biocompatibility thereof, in particular a biocompatibility that is higher than that of the film made of polyethylene. The film according to the invention has been tested with respect to its functional and mechanical properties. The results are reported in the herebelow table in comparison with a polyethylene film. In the table are also listed figures relating to a film according to the invention which has been coated with 0.5% by weight of a surfactant consisting of low molecular polytehylenglycol (Mw < 600).

Mechanical and functional tests

	Unit	Method	Polyethylene	NF 866	Mater-Bi® NF806 + surfactant
Grammage	g/m^2	ASTM D3776	22	25.6	27
Ultimate tensile strength	N/m^2	ASTM D 882	14	10	15
Ultimate elongation MD	%	ASTM D 882	85	103	130
Stress to produce 5% elongation MD	N/m^2	ASTM D 882	4.20	3.5	3.9
Wetback	g	EDANA 151.3	0.06	0.06	0.09
Strike-through time	s	EDANA 150.5	2.9	3.5	2.7
Open area	%	TFPI	23	15	34
Run off	g	EDANA 152.1-02	3.1	1.1	0

CLAIMS

1. Perforated biodegradable film comprising:
   - at least one aliphatic or aliphatic-aromatic biodegradable polyester obtained from a dicarboxylic or hydroxy acid and a diol;
   - at least one polysaccharide derivative.
2. Perforated biodegradable film according to claim 1, wherein said polysaccharide derivative is starch.
3. Perforated biodegradable film according to claim 2, wherein said starch is maize starch.
4. Perforated biodegradable film according to claim 1, wherein said biodegradable polyester is an aliphatic-aromatic polyester of the dicarboxylic acid -diol type.
5. Perforated biodegradable film according to claim 4, wherein said aliphatic-aromatic polyester is linear or branched co-terephthalate polybutylene adipate.
6. Perforated biodegradable film according to any of the preceding claims, characterised by an open area comprised between 5% and 75%.
7. Perforated biodegradable film according to claim 6, characterised by an open area comprised between 10% and 65%.
8. Perforated biodegradable film according to claim 7, characterised by an open area comprised between 15% and 55%.
9. Perforated biodegradable film according to any of the claims from 1 to 5, characterised by a hole density comprised between 10 and 200 holes/cm^2.
10. Perforated biodegradable film according to claim 9, characterised by a hole density comprised between 30 and 150 holes/cm^2.
11. Perforated biodegradable film according to claim 10, characterised by a hole density comprised between 50 and 120 holes/cm^2.
12. Perforated biodegradable film according to claims from 6 to 11, wherein the perforation is a hot perforation performed under vacuum conditions with production of conical holes.
13. Sanitary article comprising the perforated biodegradable film according to any of the preceding claims.
14. Sanitary article according to claim 13, wherein said biodegradable film is an internal film or topsheet intended to be in contact with the skin of a user.
15. Sanitary article according to claim 13, wherein said biodegradable film is an internal

film or topsheet, characterised by further comprising a breathable and complete-biological-barrier film made of a biodegradable material as outer film or backsheet.

16. Sanitary article according to claim 15, wherein said breathable and complete-biological-barrier film made of a biodegradable material is a starch-based film.

17. Use of the perforated biodegradable film according to any of claims 1-12 as absorbent for packaging foodstuffs releasing liquids.

INTERNATIONAL SEARCH REPORT

PCT/EP2005/005495

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J5/18 C08L67/02 A61L15/22 C08L3/00

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 C08J C08L A61L

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	DE 100 54 650 A1 (BASF AG) 8 May 2002 (2002-05-08) paragraph '0009! - paragraph '0042! paragraph '0080! - paragraph '0084! paragraph '0092! - paragraph '0094! paragraph '0098! - paragraph '0099!; claims 1,2	1-5, 13-16 6-12
X	US 5 417 679 A (TOMS ET AL) 23 May 1995 (1995-05-23) column 2, line 54 - column 3, line 13 column 5, line 45 - column 6, line 13 column 9, line 56 - column 10, line 9 column 11, line 54 - line 63; examples 1,4	1-17

-/--

[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
27 September 2005	06/10/2005

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	Contet, F

INTERNATIONAL SEARCH REPORT

PCT/EP2005/005495

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	WO 03/089490 A (NOVAMONT S.P.A; BASTIOLI, CATIA; CELLA, GIANDOMENICO; DELTREDICI, GIAN) 30 October 2003 (2003-10-30) page 2, line 10 - page 5, line 7 page 6, line 18 - page 7, line 12; claims 1-23 -----	1-5,13, 17 6-12, 14-16
X	EP 1 116 748 A (YOSHIHARA, TOSHINOBU) 18 July 2001 (2001-07-18) paragraph ‘0011! - paragraph ‘0015! paragraph ‘0040! - paragraph ‘0044! paragraph ‘0054! - paragraph ‘0059! paragraph ‘0063! paragraph ‘0085!; figure 3 -----	1-5

INTERNATIONAL SEARCH REPORT

PCT/EP2005/005495

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
DE 10054650	A1	08-05-2002	NONE			
US 5417679	A	23-05-1995	AT	147995	T	15-02-1997
			AU	668356	B2	02-05-1996
			AU	2260292	A	25-01-1993
			BR	9206214	A	13-12-1994
			CA	2111241	A1	07-01-1993
			CZ	9302881	A3	13-07-1994
			DE	69217063	D1	06-03-1997
			DE	69217063	T2	15-05-1997
			DK	595859	T3	11-08-1997
			EP	0595859	A1	11-05-1994
			ES	2096763	T3	16-03-1997
			FI	935819	A	04-02-1994
			GR	3022366	T3	30-04-1997
			HK	1006423	A1	26-02-1999
			HU	68435	A2	28-06-1995
			IE	922064	A1	30-12-1992
			JP	3280972	B2	13-05-2002
			JP	6508776	T	06-10-1994
			KR	214922	B1	02-08-1999
			MX	9203309	A1	01-12-1992
			PH	30498	A	28-05-1997
			PL	169131	B1	28-06-1996
			PT	8541	U	31-03-1993
			PT	101703	A	31-01-1996
			SG	55032	A1	21-12-1998
			SK	147793	A3	07-09-1994
			WO	9300116	A1	07-01-1993
WO 03089490	A	30-10-2003	AU	2003239816	A1	03-11-2003
			CA	2481843	A1	30-10-2003
			CN	1646630	A	27-07-2005
			EP	1497370	A2	19-01-2005
			IT	MI20020865	A1	22-10-2003
			JP	2005523354	T	04-08-2005
			US	2005054813	A1	10-03-2005
EP 1116748	A	18-07-2001	AU	5064999	A	06-03-2000
			CN	1312836	A	12-09-2001
			WO	0009609	A1	24-02-2000
			TW	593531	B	21-06-2004
			US	6437022	B1	20-08-2002