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(54) Title: HEAT SEALABLE PACKAGING MATERIAL COMPRISING MICROFIBRILLATED CELLULOSE AND PRODUCTS MADE THEREFROM

(57) Abstract: The present invention is directed to a packaging material comprising a layer of microfibrillated cellulose (MFC) and an aluminium layer having a thickness of 0.1-20 µm, wherein the layer comprising MFC and/or the aluminium layer has been laminated or extrusion coated on at least one side with a thermoplastic polymer and wherein the amount of aluminium is sufficient to make the packaging material heat sealable by induction. The MFC layer contains at least 60% by weight of microfibrillated cellulose.



HEAT SEALABLE PACKAGING MATERIAL COMPRISING
MICROFIBRILLATED CELLULOSE AND PRODUCTS MADE THEREFROM

Technical field

The present invention is directed to a packaging material comprising a layer
5 of microfibrillated cellulose (MFC) and an aluminium layer having a thickness
of 0.1-20 μm , wherein the layer comprising MFC and/or the aluminium layer
has been laminated or extrusion coated on at least one side with a
thermoplastic polymer and wherein the amount of aluminium is sufficient to
make the board heat sealable by induction. The MFC layer contains at least
10 60% by weight of microfibrillated cellulose.

Background

15 Packages used for sensitive objects such as liquid beverages need to have
sufficient barrier properties. Typically, aluminium is used for these purposes
and generally provides sufficient properties with regard to penetration of gas,
such as oxygen. The aluminium layer is also an aroma barrier and plays an
important function in heat sealing.

20

Induction is commonly used as a means to heat seal packages. This is based
on the presence of a sufficient amount of conductive material to achieve the
heat sealable properties.

25 One issue with the use of aluminium is that it poses an environmental
challenge and it would be desirable to replace aluminium with renewable
materials. However, it is essential to maintain the barrier properties of the

material to the extent it is to be used in packages for e.g. liquids and it is also important that the material is sufficiently crack-resistant.

5 Summary of the invention

It has surprisingly been found that by using a layer of microfibrillated cellulose (MFC) and an aluminium layer and wherein the layer comprising MFC and/or the aluminium layer has been laminated or extrusion coated on at least one side with a thermoplastic polymer, it is possible to achieve a packaging material suitable for heat sealing using induction even with a very small amount of aluminium. Surprisingly, the packaging material comprising MFC provides sufficient barrier properties even at high humidity.

15 The present invention is thus directed to a packaging material comprising a layer of MFC and an aluminium layer having a thickness of 0.1-20 μm , wherein the layer comprising MFC and/or the aluminium layer has been laminated or extrusion coated on at least one side with a thermoplastic polymer and wherein the amount of aluminium is sufficient to make the board
20 heat sealable by induction.

In one embodiment, a thermoplastic polymer has been laminated on both sides of the MFC layer.

25 The aluminium layer used in accordance with the present invention is continuous. The thickness of the aluminium layer is 0.1-20 μm , such as 0.2-15 μm or 0.3-10 μm or 0.6-10 μm or 0.5-3.5 μm , such as 1-3 μm , such as 1.2-28 μm . In one embodiment of the present invention, the amount of aluminium is in the range of from 1g to 30g per m^2 finished packaging material, such as
30 from 3g to 10 g per m^2 finished packaging material. The thickness of the aluminium layer can be determined by methods known in the art, such as by measuring optical density.

In one embodiment of the present invention, the oxygen transmission rate (OTR) of the MFC layer is less than 20 cc/m²*day, preferably less than 15 cc/m²*day measured at standard conditions (50%RH, 23°C), at a grammage
5 of 10-50 gsm. The OTR can be determined using methods known in the art.

In one embodiment of the present invention, the oxygen transmission rate (OTR) of the packaging material according to the present invention, i.e. the final product to be used in a package, is less than 5 cc/m²*day, preferably
10 less than 3 cc/m²*day or less than 1.5 cc/m²*day measured at standard conditions (50%RH, 23°C). The OTR can be determined using methods known in the art.

The packaging material according to the present invention can be subjected
15 to printing through a reel to reel or reel to sheet or sheet fed printing process, but can also be subjected to off-line surface treatment with other technologies such as flexogravure, rotogravure, reverse rotogravure, silk screen printing, inkjet printing, offset printing (lithography), spray, curtain, foam or other printing or surface treatment techniques.

20 Depending on the amount of aluminium used, the packaging material according to the present invention may be biodegradable and/or compostable. In this context, compostability is defined in accordance with ISO 18606, i.e. constituents in the whole material which are present at
25 concentrations of less than 1% do not need to demonstrate biodegradability. However, the sum of such constituents shall not exceed 5%. Biodegradability is defined as follows: the ultimate aerobic biodegradability shall be determined for the whole material or for each organic constituent which is present in the material at a concentration of more than 1% (by dry mass).
30 Constituents present at levels between 1 to 10% shall be tested individually.

Detailed description

5

The microfibrillated cellulose used according to the present invention can be prepared using methods known in the art.

10 In one embodiment of the present invention, the MFC layer is formed in a paper making machine or according to a wet laid production method, by providing a suspension onto a wire and dewatering the web to form an intermediate thin substrate or said film. A suspension comprising microfibrillated cellulose is provided to form said film.

15 In one embodiment of the present invention, the MFC layer used in accordance with the present invention can be made according to any known processes described in the art such as wet laid methods, printing, extrusion, lamination etc.

20 Microfibrillated cellulose (MFC) shall in the context of the patent application mean a nano scale cellulose particle fiber or fibril with at least one dimension less than 100 nm. MFC comprises partly or totally fibrillated cellulose or lignocellulose fibers. The liberated fibrils have a diameter less than 100 nm, whereas the actual fibril diameter or particle size distribution and/or aspect
25 ratio (length/width) depends on the source and the manufacturing methods.

The smallest fibril is called elementary fibril and has a diameter of approximately 2-4 nm (see e.g. Chinga-Carrasco, G., *Cellulose fibres, nanofibrils and microfibrils, The morphological sequence of MFC components from a plant physiology and fibre technology point of view, Nanoscale research letters* 2011, 6:417), while it is common that the
30 aggregated form of the elementary fibrils, also defined as microfibril (Fengel, D., *Ultrastructural behavior of cell wall polysaccharides, Tappi J.*, March 1970,

Vol 53, No. 3.), is the main product that is obtained when making MFC e.g. by using an extended refining process or pressure-drop disintegration process. Depending on the source and the manufacturing process, the length of the fibrils can vary from around 1 to more than 10 micrometers. A coarse
5 MFC grade might contain a substantial fraction of fibrillated fibers, i.e. protruding fibrils from the tracheid (cellulose fiber), and with a certain amount of fibrils liberated from the tracheid (cellulose fiber).

There are different acronyms for MFC such as cellulose microfibrils, fibrillated
10 cellulose, nanofibrillated cellulose, fibril aggregates, nanoscale cellulose fibrils, cellulose nanofibers, cellulose nanofibrils, cellulose microfibers, cellulose fibrils, microfibrillar cellulose, microfibril aggregates and cellulose microfibril aggregates. MFC can also be characterized by various physical or physical-chemical properties such as large surface area or its ability to form a
15 gel-like material at low solids (1-5 wt%) when dispersed in water. The cellulose fiber is preferably fibrillated to such an extent that the final specific surface area of the formed MFC is from about 1 to about 300 m²/g, such as from 1 to 200 m²/g or more preferably 50-200 m²/g when determined for a freeze-dried material with the BET method.

20

Various methods exist to make MFC, such as single or multiple pass refining, pre-hydrolysis followed by refining or high shear disintegration or liberation of fibrils. One or several pre-treatment step is usually required in order to make MFC manufacturing both energy efficient and sustainable. The cellulose
25 fibers of the pulp to be supplied may thus be pre-treated enzymatically or chemically, for example to reduce the quantity of hemicellulose or lignin. The cellulose fibers may be chemically modified before fibrillation, wherein the cellulose molecules contain functional groups other (or more) than found in the original cellulose. Such groups include, among others, carboxymethyl
30 (CM), aldehyde and/or carboxyl groups (cellulose obtained by N-oxyl mediated oxydation, for example "TEMPO"), or quaternary ammonium (cationic cellulose). After being modified or oxidized in one of the above-

described methods, it is easier to disintegrate the fibers into MFC or nanofibrillar size fibrils.

The nanofibrillar cellulose may contain some hemicelluloses; the amount is
5 dependent on the plant source. Mechanical disintegration of the pre-treated
fibers, e.g. hydrolysed, pre-swelled, or oxidized cellulose raw material is
carried out with suitable equipment such as a refiner, grinder, homogenizer,
colloider, friction grinder, ultrasound sonicator, fluidizer such as microfluidizer,
macrofluidizer or fluidizer-type homogenizer. Depending on the MFC
10 manufacturing method, the product might also contain fines, or
nanocrystalline cellulose or e.g. other chemicals present in wood fibers or in
papermaking process. The product might also contain various amounts of
micron size fiber particles that have not been efficiently fibrillated.

MFC is produced from wood cellulose fibers, both from hardwood or softwood
15 fibers. It can also be made from microbial sources, agricultural fibers such as
wheat straw pulp, bamboo, bagasse, or other non-wood fiber sources. It is
preferably made from pulp including pulp from virgin fiber, e.g. mechanical,
chemical and/or thermomechanical pulps. It can also be made from broke or
recycled paper.

20 The above described definition of MFC includes, but is not limited to, the new
proposed TAPPI standard W13021 on cellulose nanofibril (CNF) defining a
cellulose nanofiber material containing multiple elementary fibrils with both
crystalline and amorphous regions.

25 According to another embodiment, the suspension may comprise a mixture of
different types of fibers, such as microfibrillated cellulose, and an amount of
other types of fiber, such as kraft fibers, fines, reinforcement fibers, synthetic
fibers, dissolving pulp, TMP or CTMP, PGW, etc.

30 The suspension may also comprise other process or functional additives,
such as fillers, pigments, wet strength chemicals, dry strength chemicals,

retention chemicals, cross-linkers, softeners or plasticizers, adhesion primers, wetting agents, biocides, optical dyes, fluorescent whitening agents, de-foaming chemicals, hydrophobizing chemicals such as AKD, ASA, waxes, resins etc. Additives can also be added using a size press.

5

There are several methods for preparing a film of MFC, including wire forming and cast forming. In wire forming, a suspension, comprising microfibrillated cellulose, is dewatered on a porous surface to form a fibrous web. A suitable porous surface is e.g. wire in a paper machine. The fibrous web is then dried
10 in a drying section in a paper machine to form the MFC film, wherein the film has a first side and a second side. The papermaking machine that may be used in the process according to the present invention may be any type of machine known to the skilled person used for the production of paper, paperboard, tissue or similar products, alternatively for example a modified or
15 non-conventional papermaking machine.

The furnish is placed onto the wire and then a web is formed, which may be dewatered to form an intermediate thin substrate or film.

In cast forming, the suspension, comprising MFC, is applied on a supporting
20 medium with a non-porous surface. The non-porous surface is e.g. a plastic or metal belt on which the suspension is evenly spread and the MFC film is formed during drying. The MFC film is then peeled off from the supporting medium in order to form a stand-alone film, wherein the film has a first side and a second side.

25

According to the present invention, the MFC layer and/or the aluminium layer is laminated or extrusion coated or dispersion coated with a thermoplastic polymer. The thermoplastic film typically has a glass transition temperature (T_g) of from 70°C to 200°C. In one embodiment of the present invention, the
30 thermoplastic polymer is selected from polyethylene (PE), polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), linear-low density polyethylene (LLDPE), polylactic acid (PLA), polyglycolide

(PGA), ethylene vinyl acetate (EVA), ethylene vinyl alcohol (EVOH), polyamide (PA), ionomers (e.g. Surlyn) or combinations thereof. The thermoplastic film is typically present at at least 5 g/m², such as at least 15 g/m², such as at least 20 g/m² or at least 30 g/m².

5

In one embodiment of the present invention, the MFC layer is laminated with the thermoplastic polymer. The lamination can be carried out using methods known in the art.

10 The amount of aluminium in the aluminium layer according to the present invention is such that it is sufficient to make the packaging material heat sealable using induction. The heat sealing can be performed using methods and equipment known in the art.

15 A final liquid packaging board comprising the packaging material according to the present invention may comprise several layers. In one embodiment, the product has the following structure: PE/board/MFC/Al/PE, i.e. the layers are the following: a polyethylene (PE) layer, a layer of a conventional board material, a layer of microfibrillated cellulose MFC, an aluminium layer with an
20 amount of aluminium sufficient to make the product heat sealable by induction, and a layer of PE. In one embodiment, the product has the following structure: PE/board/Al/MFC/PE, i.e. the layers are the following: a polyethylene (PE) layer, a layer of a conventional board material, a layer of aluminium, a layer of microfibrillated cellulose MFC, and a layer of PE. In one
25 embodiment, the product has the following structure:

PE/board/PE/MFC/Al/PE, i.e. the layers are the following: a polyethylene (PE) layer, a layer of a conventional board material, a layer of polyethylene (PE), a layer of microfibrillated cellulose MFC, an aluminium layer and a layer of PE. A person skilled in the art would recognize that other structures are possible.

30 The grammage of a structure as described above is typically in the range of 180-500 g/m².

In view of the above detailed description of the present invention, other modifications and variations will become apparent to those skilled in the art. However, it should be apparent that such other modifications and variations may be effected without departing from the spirit and scope of the invention.

CLAIMS

1. A packaging material comprising a layer that comprises at least 60%
5 by weight of microfibrillated cellulose and an aluminium layer having a thickness of 0.1-20 μm , wherein the layer comprising microfibrillated cellulose and/or the aluminium layer is laminated or extrusion coated with a thermoplastic polymer and wherein the amount of aluminium is sufficient to make the packaging material heat sealable by induction.
10
2. The material according to claim 1, wherein said layer comprising microfibrillated cellulose has been laminated with a thermoplastic polymer.
- 15 3. The material according to claim 2, wherein said thermoplastic polymer is polyethylene.
4. The material according to claim 1, wherein said layer comprising microfibrillated cellulose has been extrusion coated with a
20 thermoplastic polymer.
5. The material according to claim 4, wherein said thermoplastic polymer is polyethylene.
- 25 6. The material according to any one of claims 1-5, wherein the amount of aluminium is in the range of from 1g to 30g per m^2 finished packaging material, such as from 3g to 10 g per m^2 finished packaging material.
- 30 7. A method of manufacturing a packaging material according to any one of claims 1-6, comprising the steps of
 - a) preparing a layer of microfibrillated cellulose;

- b) providing an aluminium layer having a thickness of 0.1-20 μm ,
comprising aluminium in an amount sufficient for the material to be
heat sealable by induction;
- c) combining the layers of step a) and b);
- 5 d) laminating or extrusion coating the layer of step a) or b) with a
thermoplastic polymer on at least one side of said layer.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2018/052132

A. CLASSIFICATION OF SUBJECT MATTER

IPC: see extra sheet

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: B32B, C08J, D21H

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

SE, DK, FI, NO classes as above

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

EPO-Internal, PAJ, WPI data, BIOSIS, COMPENDEX, MEDLINE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2017046754 A1 (STORA ENSO OYJ), 23 March 2017 (2017-03-23); page 8, line 36 - page 9, line 13; page 10, line 8 - page 10, line 17; claim 1 --	1-7
Y	EP 2451644 B1 (TETRA LAVAL HOLDINGS & FINANCE), 16 May 2012 (2012-05-16); paragraphs [0015], [0023], [0048]-[0053], [0073], [0113], [0125]; figures 1a-d; claim 1 --	1-7
A	JP 2015024540 A (TOPPAN PRINTING CO LTD), 5 February 2015 (2015-02-05); paragraphs [0003], [0027]-[0028], [0033]-[0038], [0042]-[0043]; figures --	1-7



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

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 20120251818 A1 (AXRUP LARS ET AL), 4 October 2012 (2012-10-04); paragraphs [0007], [0010]-[0013], [0029]; claims 1,4 --	1-7
A	US 20130004687 A1 (OOMORI YUMIKO ET AL), 3 January 2013 (2013-01-03); paragraphs [0047], [0076]-[0078], [0082]-[0083]; figures --	1-7
A	US 20130260143 A1 (OOMORI YUMIKO ET AL), 3 October 2013 (2013-10-03); paragraphs [0012]-[0017], [0088]-[0093] -- -----	1-7

Continuation of: second sheet

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2018/052132

WO	2017046754 A1	23/03/2017	CA	2995437 A1	23/03/2017
			CN	108026696 A	11/05/2018
EP	2451644 B1	16/05/2012	BR	112012000407 A2	05/04/2016
			CN	102470649 A	23/05/2012
			RU	2012104237 A	20/08/2013
			RU	2540605 C2	10/02/2015
			WO	2011003566 A8	12/01/2012
JP	2015024540 A	05/02/2015	JP	6318490 B2	09/05/2018
US	20120251818 A1	04/10/2012	AU	2010334982 B2	20/11/2014
			BR	112012015636 A2	10/05/2016
			CA	2784232 A1	30/06/2011
			CN	102686399 A	19/09/2012
			CN	107097503 A	29/08/2017
			EP	2516156 A4	13/08/2014
			JP	6122909 B2	26/04/2017
			JP	2013514906 A	02/05/2013
			JP	2016000526 A	07/01/2016
			NZ	600301 A	27/06/2014
			RU	2012130946 A	27/01/2014
			RU	2543206 C2	27/02/2015
			SE	0950995 A1	22/06/2011
			SE	534932 C2	21/02/2012
			WO	2011078770 A1	30/06/2011
			ZA	201204190 B	27/02/2013
US	20130004687 A1	03/01/2013	CN	102834259 B	20/01/2016
			EP	2551105 A4	18/09/2013
			JP	5772815 B2	02/09/2015
			JP	WO2011118521 A1	04/07/2013
			KR	101816331 B1	08/01/2018
			KR	20130010476 A	28/01/2013
			WO	2011118521 A1	29/09/2011
US	20130260143 A1	03/10/2013	CN	103052499 B	20/01/2016
			EP	2644371 A4	28/06/2017
			JP	WO2012070441 A1	19/05/2014
			JP	5928339 B2	01/06/2016
			KR	20130140627 A	24/12/2013
			US	9404016 B2	02/08/2016
			WO	2012070441 A1	31/05/2012