SAMPLE LANDSCAPE STUDY- POLYETHYLENE FURANOATE (PEF)
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✓ Key Developments Related to Bio-Based polymers
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Introduction- Polyethylene Furanoate (PEF)

What is PEF?

• PEF is a 100% recyclable bio-based polymer derived from plants having the potential to replace the plastic industry’s giant polyethylene terephthalate (PET), which is a durable material derived from conventional resources.
• It can be referred as the next generation polyester, having better mechanical and barrier properties than the current biggest selling polyester (PET).

PEF V/S PET

1) PEF has very good barrier properties (hard to achieve with most bio-based polymers)
   • O2 barrier – 6 times greater than PET
   • CO2 barrier – 3 times better than PET
   • H2O barrier – 2 times better than PET
2) Better tensile strength
3) PEF requires less additives than PET

For sources of information, please refer to Appendix 1
4) PEF also has interesting mechanical properties compared to PET.
   • Higher Tg (glass transition temperature)
   • Lower Tm (melting point)
   • Higher modulus

5) PEF can be recycled and incorporated into the PET recycle streams at up to 5% PEF with no
   affect on the recycled PET performance.

6) Permits greater light weighting and superior thermal stability without heat-setting (can be hot filled
   at about 200-deg F).

Applications of PEF

• PEF Bottles- Water bottle, beverage bottle etc
• PEF Fibers- Apparels, carpets, home furnishing, disposables commodities, fabrics, diapers, filters
  and industrial fibres
• PEF Films

For sources of information, please refer to Appendix 1
• **Avantium** developed and patented YXY technology platform aimed at manufacturing bio fuels, bio based plastics and bio chemicals.

• **Avantium** established strategic partnership with **Danone, Coca-Cola and ALPLA** for developing and commercializing bio-based polymers derived from PEF.

• In 2014, **Avantium, Danone, Swire Pacific** and **Coca-Cola** signed a consortium of USD 50 million investments aimed at developing and commercializing the alternative to PET for packaging applications.

• In 2014, **Avantium** demonstrated the application of PEF for manufacturing of fibers to make 100% bio based t-shirts for textile manufacturers.

• Asia Pacific is likely to be a lucrative market in the near future on account of growing packaging industry in India and China in vague of positive outlook on food & beverage, consumer goods and pharmaceutical sectors.

• North America is likely to be promising market for bio based chemicals in light of increasing environmental concerns towards reducing GHG emissions coupled with stringent regulations towards non-recyclable plastic consumption at domestic level.

For sources of information, please refer to **Appendix 1**
Key Developments Related To Bio-Based Polymers

- **2009**
  - PlantBottle™ by Coca-Cola (DTCC) - first ever recyclable PET beverage bottle introduced in the market

- **June 2011**
  - Toray - Gevo partnership succeeded in producing fully renewable biobased PET

- **Dec 08 2011**
  - Avantium officially opened PEF pilot plant in Geleen, Netherlands

- **Dec 15 2011**
  - Coca-Cola announced its agreement with Virent, Gevo and Avantium, companies which are plant based polymer manufacturers

- **June 2012**
  - Coca-Cola, Ford, Heinz, NIKE, and P & G announced the formation of Plant PET Technology Collaborative (PTC), for development and use of 100% plant-based PET materials and fibre

- **2014**
  - Avantium closed a financing round of $50 million from a consortium of Swire Pacific, Coca-Cola, DANONE, ALPLA, and existing shareholders

- **2016**
  - Avantium plans to start commercial production of FDCA and PEF in 2016 through a 50,000 tons/year plant

For sources of information, please refer to Appendix 1
Objectives of the Landscape/Study

- To understand technology and prepare patent landscape
- To understand major patent holders, geographical distribution of patents, top sub-technologies based on IPC codes
- Analysis of patent filing trends over the years, top assignees, top patent classifications, among others
- To conduct Patent Portfolio based study of patents relating to core focus area of PEF in the patents/applications
- To understand the recycling technology of PEF and Novelty Features of all Granted Patents pertaining to PEF

Assumptions:

- Report provides patent analysis for PEF market, which includes study of recycling of PEF, applications, and advance technology based patents
- The landscape study focuses on patents pertaining to PEF filed between 2005-2015

For sources of information, please refer to Appendix 1
Global patent filing trend analysis shows a consistent rise in the number of patent applications filed during year 2007-2012, followed by a dip in year 2013-2015. Highest rise was observed in the year from 2011-2012. Maximum number of applications were filed from WO, followed by US and CN jurisdictions.

# Graphs were prepared based on the analysis of application year for all published applications (family expanded data)
# Geographic Filing Trend analysis was done based on the application country.
Filing trend of last 10 years for top 13 Assignees (based on representative family members) show a significant rise in filing from 2010-2012 with NOVAMONT leading the pack in 2010, and P&G in 2011 and 2012.

# Graph was prepared based on the analysis of application year for published applications (based on the representative family numbers)
Global patent application publication trend presents a significant increase in the number of publication during last decade with its peak at 2014 which suggests significant filing during 2010-2013. Total number of patents published in 2015 may increase till the end of the year.

# Graph was prepared based on the analysis of publication year for all published applications (family expanded data)
Overall Top Assignees

Procter & Gamble is among leading patent filers in PEF Technology, followed by Canon, which also has a significant patent portfolio.

# The graph was prepared taking into considerations all Mergers & Acquisitions.
Top Inventors

As evident, Tanaka Yuchiro from Canon is among leading inventors in PEF Technology. Number two position is shared by inventors from P&G, Evian Eaux and Furanix.
Top International Patent Classifications (IPCs)

Maximum number of applications filed during 2010-2015 correspond to IPC class C08G relating to ‘macromolecular compounds obtained otherwise than by reactions only involving carbon-to-carbon unsaturated bonds’. Amongst applications filed in C08G, 22% of applications were filed in technology of sub-class C08G 63/16 which relates to ‘Dicarboxylic acids and dihydroxy compounds’. Second highest number of applications were filed in the technology covered by IPC class B32B which relates to ‘layered products, i.e. products built-up of strata of flat or non-flat, e.g. cellular or honeycomb, form’. Amongst applications filed in B32B, 37% of applications were filed in technology of sub-class B32B 27/08 which relates to the ‘Organic chemistry; Heterocyclic Compounds; Carbon atoms having three bonds to hetero atoms with at the most one bond to halogen’.

# For IPC sub-class definitions please refer to Appendix 2.
Geographic Origin of Innovation

Insights

Analysis of Geographic Origin of Innovation demonstrates that maximum number of innovations originates from US followed by CN and JP jurisdictions. P&G contributes to maximum number of innovations originating from US. Universities and CHANGCHUN APPLIED CHEMISTRY in particular contributes to maximum number of innovations originating from CN. Canon contributes to maximum number of innovations originating from JP.

# The graph representing Geographic origin of innovation was prepared based on the analysis of priority country
Key Technological Trends
Maximum percentage of applications were filed where PEF is used in packaging materials, followed by this is fibers and fibrous webs where second highest number of applications were filed relating to PEF. Procter & gamble is the main player in the applications directed towards using PEF in the packaging material. Toray is dominating applicant in the applications directed towards using PEF in the fibers and fibrous webs. Evian Eaux and Toray are having maximum percentages of applications filed against their names in the field of bottles and films respectively. Procter & Gamble is the only player who has filed patent applications which are directed to using PEF in disposable articles.
PEF Compositions/Derivatives with desired properties

Variations in Diol components to get PEF or its different derivatives

2-amino-2-methyl-1,3-Propanediol (AMPD) + Ethylene Glycol

PEF or its Derivative

US8981037
Canon

US9102793
Canon

Ethylene Glycol + Diethylene Glycol (DEG)

Different Technologies to achieve PEF with desired properties

Mixing components in specific ratio to get Polymers having specific melt flow index

PEF with Desired Properties

US8846825
Novamont

CN103502303
Toray

Mixing components in specific ratio to get Polymers having specific melt flow index
Patent Portfolio Analysis
Company Profile
Avantium is a leading technology company specialized in the area of advanced catalytic research with groundbreaking innovation as its primary goal. It achieves this through two distinct propositions: Catalysis and YXY.

Technological Dissection of Patent Portfolio

- Process for preparation of PEF: 72%
- Process for Recycling: 14%
- Application in Fibre: 14%

Patent Portfolio Analysis – Furanix (Avantium)
Key developments

- Avantium completed a $36M million financing
- Avantium entered in agreement with Coca-cola for production of bio-based polymers
- Announcement of Avantium – Rhodia partnership
  Avantium – Solvay to jointly develop a next generation of green high-performance polyamides
- Avantium announced partnership with ALPLA and DANONE
- Avantium closed a financing round of $50 million from a consortium of Swire Pacific, Coca-Cola, DANONE, ALPLA, and existing shareholders
- Avantium plans to start commercial production of FDCA and PEF in 2016 through a 50,000 tons/year plant

For sources of information, please refer to Appendix 1
# Key Patents:

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Novel Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>US9073886</td>
<td>A process for the <strong>depolymerization</strong> of a furandicarboxylate containing polyester, which process comprises <strong>reacting the polyester with an alcohol or water in the presence of a depolymerisation catalyst to yield a product comprising a furandicarboxylate compound and diol.</strong></td>
</tr>
<tr>
<td>US8338626</td>
<td>A method for the manufacture of ethers of 5-hydroxymethylfurfural by reacting a glucose-containing starting material with an alcohol, selected from methanol, ethanol and mixtures thereof, in the presence of a catalytic or sub-stoichiometric amount of an acid catalyst</td>
</tr>
<tr>
<td>IN265547</td>
<td>Method for the <strong>manufacture of ethers of 5-hydroxymethyl furfural</strong> by reacting a fructose and/or glucose-containing starting material with an alcohol in the presence of a catalytic or sub-stoichiometric amount of a heterogeneous or homogeneous acid catalyst, wherein water is present as solvent in addition to the alcohol, and wherein the method is performed in a continuous flow process at a temperature from 125 to 300°C.</td>
</tr>
<tr>
<td>CA2644409</td>
<td>Method for the manufacture of ethers of 5-hydroxymethyl furfural by reacting a starting material containing at least one of fructose and glucose, with an alcohol in the presence of a catalytic or sub-stoichiometric amount of a heterogeneous or homogeneous acid catalyst, wherein water is present as solvent in addition to the alcohol, and wherein the method is performed in a continuous flow process at a temperature from 125 to 300°C.</td>
</tr>
<tr>
<td>EA021670</td>
<td>Method for the manufacture of 5-hydroxymethylfurfural ethers by reacting a fructose and/or glucose-containing starting material with an alcohol selected from methanol and ethanol in the presence of a catalytic or sub-stoechiometric amount of a heterogeneous or homogeneous acid catalyst</td>
</tr>
<tr>
<td>JP5738517</td>
<td>Method for the manufacture of 5-alkoxymethylfurfural derivatives by reacting a glucose-containing starting material with an alcohol in the presence of a catalytic or sub-stoechiometric amount of acid catalyst.</td>
</tr>
</tbody>
</table>

# All granted patents were analysed irrespective of their INPADOC families.
Company Profile
Procter & Gamble Co., also known as P&G, is an American multinational consumer goods company which is active into areas such as beauty care, baby, feminine, and family care, fabric and home care, health and grooming. It is mainly active into Europe, America, IMEA and Asia.

Technological Dissection of Patent Portfolio

Application in Disposable Articles
- EP2685951
- EP2685952
- US20120238982
- US20120238979

Application in Packaging Materials
- US20140377512
- EP2697062
- EP2763908

Application in Fibrous Webs
- US20130023608
- EP2668105
- US20120238170
- US20120237718

- Fibrous Webs 36.3%
- Disposable Articles 36.3%
- Packaging Material 27.3%
### Key Patents:

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Novel Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN103429278</td>
<td>A disposable absorbent article having a structured fiber web using ASTM D6866-10, from about 10% to about 100% by Method B biobased content</td>
</tr>
<tr>
<td>US8657596</td>
<td>An apparatus comprising two intermeshing counter-rotating rolls that form a nip there between, said apparatus comprising: a) a generally cylindrical first roll; and b) a generally cylindrical second roll</td>
</tr>
<tr>
<td>US8871319</td>
<td>A flexible barrier package wherein the package exhibits a lamination strength of sealant to outer substrate of at least about 1.0 N per 25.4 mm of sample width after the package is filled to three-quarters of its volume with a laundry powder composition a and placed in a room at 50% relative humidity (RH) at 55° C. for at least about one month</td>
</tr>
</tbody>
</table>

# All granted patents were analysed irrespective of their INPADOC families.
Company Profile

Societe des Eaux Minerales d'Evian SA provides bottled mineral water. The company was incorporated in 1970 and is based in Evian-les-Bains, France. Societe des Eaux Minerales d'Evian SA operates as a subsidiary of Danone.

Technological Dissection of Patent Portfolio – Application of PEF

# No granted patents filed between year 2005-2015 are assigned to Evian Eaux Minerales.
Company Profile

Canon Inc. is a Japanese multinational specialized in the manufacture of imaging and optical products. Reportedly at the beginning of 2015, Canon was the tenth largest public company in Japan when measured by market capitalization.

Technological Dissection of Patent Portfolio

- Process of preparation of modified PEF: 12.5%
- Application in Film: 12.5%
- PEF Composition/Blend: 75%
**Key Patents:**

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Novel Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>US8143355</td>
<td>Reacting a furandicarboxylic acid compound with the polyhydric alcohol presence of an organometallic compound selected from the group consisting of tin, lead and titanium or a tetravalent hafnium</td>
</tr>
<tr>
<td>US9102793</td>
<td>A polyester resin having a number average molecular weight is 100,000 to 120,000</td>
</tr>
<tr>
<td>US8981037</td>
<td>A polyester resin wherein a glass transition temperature of the polyester resin is 93° C. or more to 109° C. or less, and wherein the polyester resin has a number average molecular weight of 31,000 to 160,000</td>
</tr>
</tbody>
</table>

# All granted patents were analysed irrespective of their INPADOC families.
Toray Industries, Inc. is a multinational company headquartered in Japan was initially into fibers and textiles, as well as plastics and chemicals. The company’s presence can also be felt in the areas such as pharmaceuticals, biotechnology and R&D, medical products, reverse osmosis membranes, electronics, IT-products, housing and engineering, and other advanced composite materials.

| Application in Disposable Articles | EP2685951 | EP2685952 | US20120238982 | US20120238979 |
| Application in Fibrous Webs | US20130023608 | EP2668105 | US20120238170 | US20120237718 |

<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Novel Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN103502303</td>
<td>Use of 1,2-propanediol with a content of 45-1000 ppm glycol.</td>
</tr>
</tbody>
</table>

# All granted patents were analysed irrespective of their INPADOC families.
PEF Recycling Technologies
Figures estimate that around ten million tons of plastic bottles need to be recycled.

Currently, less than 10% of collected plastic is recycled.

Current recycling processes are limited to only a few types of plastic waste which:

- means materials to be recycled must have same components;

- makes it difficult to recycle complex plastics that combine a mixture of different polymers

- requires chemical or thermal recycling processes that make it impossible to retrieve same characteristics as the original product.

For sources of information, please refer to Appendix1
Chemical/Thermal Recycling - Technological Advancements

**WO2015056377 by IBM**

Alcohol having 2 to 5 carbons, an amine organocatalyst, 150 to 250° C

High purity beverage bottle grade polymers

**US9073886 by Furanix (Avantium)**

Water or alcohol (from 1 to 12 carbon atoms)

Depolymerisation catalyst (an acid catalyst, a metal compound or a base)

Furandicarboxylate compound + diol
### Carbios – Foray into Enzyme based Recycling Technology

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO2015067619</td>
<td>Polymer modifying enzyme (hydrolase or oxidase)</td>
</tr>
<tr>
<td>WO2015097104</td>
<td>Depolymerase having binding affinity to PEF</td>
</tr>
<tr>
<td>WO2014079844</td>
<td>Enzymes (cutinase, lipase, esterase)</td>
</tr>
</tbody>
</table>

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**In News**

Carbios has started production at its pilot plant in Saint-Beauzire, France, for biodegradable plastic, with a capacity of 40 kilograms per hour, using its exclusive enzyme-based technology. (Date - 27th September, 2015)

For sources of information, please refer to Appendix 1
Analysis of Key Granted Patent – Universities and Other Companies
<table>
<thead>
<tr>
<th>Patent No.</th>
<th>Novel Features</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CN102453242</strong> <em>(Dalian Institute of Chemical Physics)</em></td>
<td>A Sb2O3 catalyst and esterification reaction parameters under nitrogen at a temperature of 130-180 °C, time 1-8h; the reaction pressure 2-15mmHg, a temperature of 190-280 °C, time is 0.5-8h</td>
</tr>
<tr>
<td><strong>CN102276812</strong> <em>(CHANGCHUN APPLIED CHEMISTRY)</em></td>
<td>Addition of Tetravalent titanium compound catalyst</td>
</tr>
<tr>
<td><strong>CN103275288</strong> <em>(ZHEJIANG UNIVERSITY)</em></td>
<td>A method for preparing a biodegradable multi-block copolymer by reacting L-lactic acid in the presence of an organic acid catalyst at 160-200 °C under melt condensation 2-6 hours to a number average degree of polymerization of polylactic acid prepolymer 50-250</td>
</tr>
<tr>
<td>Patent No.</td>
<td>Novel Features</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
</tr>
<tr>
<td>CN102597050 (NOVAMONT)</td>
<td>A composition comprising derived from aliphatic dicarboxylic acids, biological polyfunctional aromatic acid and diol units biodegradable aliphatic - aromatic polyester, which is derived from a polyfunctional aromatic acid derived units comprise from at least one acid and at least one renewable source of heterocyclic aromatic acid unit</td>
</tr>
<tr>
<td>CN102639594 (NOVAMONT)</td>
<td>The composition comprising (A) at least one biodegradable aliphatic-aromatic copolyester comprised between 48 and 70 % by moles and the aliphatic dicarboxylic acids comprise: i from 51 to 95 % by moles of at least one diacid C4-C6; ii from 5 to 49 % by moles (B) at least one polymer of natural origin; wherein the concentration of (A), with respect to (A+B), is &gt; 40 % in weight, and 1.5-10g / 10min melt flow index (MFI)</td>
</tr>
<tr>
<td>US8846825B (NOVAMONT)</td>
<td>Mixture having a Melt Flow Index of 1.5-10 g/10 min</td>
</tr>
<tr>
<td>US8715524 (FUJIFILM)</td>
<td>A polishing liquid for polishing a barrier layer of a semiconductor integrated circuit comprising: a diquaternary ammonium cation; a corrosion inhibiting agent; and a colloidal silica, wherein the pH of the polishing liquid is in the range of 2.5 to 5.0</td>
</tr>
<tr>
<td>FR2985260 (NATURA)</td>
<td>Production of poly (2,5-furan dicarboxylate ethylene) by polycondensation in the presence of at least one catalyst</td>
</tr>
<tr>
<td>CN103113577 (SUZHO UHNHI CHEMICAL)</td>
<td>An alcohol-soluble copolyamide comprising 2, 5-furan dicarboxylic acid, lactam, diamine as raw materials, obtained by melt polymerization</td>
</tr>
<tr>
<td>FR2995114 (ARJOWIGGINS SECURITY)</td>
<td>A method of authenticating or identifying a secure document, this document comprising at least one securing or reinforcing element comprising at least one hydrocarbon synthetic polymer derived at least partially from plant resources, process wherein the content of biological material sourced from the element</td>
</tr>
</tbody>
</table>
APPENDIX 1: Sources

- [http://www.carbios.fr/en](http://www.carbios.fr/en)
<table>
<thead>
<tr>
<th>IPC SUB-CLASS</th>
<th>DEFINITIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C08G 63/16</td>
<td>Chemistry; Metallurgy; Organic macromolecular compounds; Their preparation or chemical working-up; Compositions based thereon; Macromolecular compounds obtained otherwise than by reactions only involving carbon-to-carbon unsaturated bonds; Dicarboxylic acids and dihydroxy compounds</td>
</tr>
<tr>
<td>C07D 307/68</td>
<td>Organic chemistry; Heterocyclic Compounds; Carbon atoms having three bonds to hetero atoms with at the most one bond to halogen</td>
</tr>
<tr>
<td>C07D 307/46</td>
<td>Organic chemistry; Heterocyclic Compounds; Doubly bound oxygen atoms, or two oxygen atoms singly bound to the same carbon atom</td>
</tr>
<tr>
<td>B65D 01/02</td>
<td>Performing Operations; Transporting; Conveying; Packing; Storing; Handling thin or filamentary material; Bottles or similar containers with necks or like restricted apertures, designed for pouring contents</td>
</tr>
<tr>
<td>C08L 67/02</td>
<td>Organic Macromolecular Compounds; Their preparation or chemical working-up; Compositions based thereon; Compositions of macromolecular compounds; Polyesters derived from dicarboxylic acids and dihydroxy compounds</td>
</tr>
</tbody>
</table>
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