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# Marketplace Opportunities for Integration of Biobased and Conventional Plastics



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Table of Contents:

	Page #
Abbreviations used for various chemicals/plastics/compounded products -----	3
Executive Summary -----	4
1. Present size and segmentation of the conventional plastics industry by volume of plastics used overall -----	5
- Thermoplastics -----	6-7
- Thermosets -----	7
2. Volumes and key performance attributes of conventional oil based plastics. used in key attractive application segments for substitution by bioplastics -----	8-18
- Drivers for Bioplastics adoption -----	8
- Bioplastics Definitions -----	9-10
- Bio based/ compostable plastics conventional plastics market targets -----	10-14
- Polystyrene targeted market size -----	11-12
- PVC targeted market size -----	12-13
- PET targeted market size -----	13-14
- Biobased or partly-biobased bioplastics non-biodegradable thermoplastics -----	14-18
- Bio polyolefins and bio PVC -----	14-15
- Bio PET and Bio PTT -----	15-16
- Bio polyamides -----	16-17
- Thermosets: Bio PU, UP and epoxies -----	17
- Non-biobased bioplastics -----	17
- Projected bioplastics market volume potential -----	18
3. State of the art in terms of developing renewable resource-based materials, their property deficiencies against oil-based incumbents, issues and potential routes to cost effectively and practically overcome these deficiencies. Such routes are those being developed today and suggestions for alternative approaches -----	19-79
A. New polymers containing renewable resource “building blocks.” -----	19-37
A.1 Aliphatic polyesters (PLA, PBS, PHA’s) -----	19-33
A.2 Polyketals, PPC, TPS -----	33-34
A.3 Non-compostable polymers: PTT, polyethylene furanoate (PEF), biobased polyamides -----	34-37
B. Conventional polymers developed either partially or completely from renewable sources -----	37-52
B.1 Cellulosics -----	37-44
B.2 Starch Blends -----	44-48
B.3 PET, PE, PP, PVC -----	48
B.4 Polyurethanes, Epoxies and Unsaturated Polyesters -----	48-51

C.	New/existing renewable “building blocks” or monomers/oligomers for new and existing polymers -----	51-79
C.1	Conventional Monomers	
C 1.1	Adipic Acid-----	52-54
C 1.2	Hexamethylene Diamine (HMD) -----	54-55
C 1.3	Glucaric Acid -----	55-57
C 1.4	Succinic Acid-----	57-62
C 1.5	Ethylene Glycol -----	62-65
C 1.6	Butane Diol (BDO) -----	65-69
C 1.7	Caprolactam-----	69-70
C 1.8	Terephthalic Acid (TPA)-----	70-73
C 1.9	Acrylic Acid -----	74-75
C.2	New Monomers -----	76-79
C 2.1	(2, 5 Furan dicarboxylic acid)-FDCA-----	76
C 2.2	Isosorbide-----	76-79
C 2.3	Propane 1,3 diol (PDO) -----	79
4.	Present size of the Bioplastics Industry and projected growth trends -----	79-88
-	Review of the major market studies for Bioplastics-----	80-86
-	Comments on Market Studies-----	86-87
-	Jim Lunt & Associates Market Assessment-----	87-88
5.	Legislative activities driving adoption of Bioplastics -----	88-96
-	Brazil -----	88-89
-	China-----	89
-	France -----	89-90
-	Germany -----	90
-	Italy-----	90-91
-	Japan-----	91-92
-	Korea-----	92
-	Malaysia-----	93
-	Netherlands -----	93
-	Norway -----	93-94
-	Sweden -----	94
-	Thailand -----	94-95
-	United Kingdom -----	95
-	United States-----	95-96
6.	Key players in bioplastics production today and going forward -----	96-113
(a)	The overall trends within the bioplastics industry in terms of single-use disposables and the increasing introduction of durable bioplastics and their chemical building blocks -----	96-101
(b)	The increasingly global nature of the industry -----	101-102
(c)	The replacement of oil as a major energy and carbon source by shale gas -----	102-104
(d)	The over reliance on food crops and developments in alternative feedstocks -----	104-113
7.	Summary and recommendations for how AURI could contribute and participate in driving the growth of the bioplastics industry-----	113-114
	Summary -----	113-114
	Specific recommendations for AURI to participate in bioplastics -----	114

**Abbreviations used for Various Chemicals/Polymers**

	Commercial Name	Abbreviation
Chemicals	diglycidyl ether of bisphenol A	DGEBA
	furan dicarboxylic acid	FDCA
	gamma-butyrolactone	GBL
	mono ethylene glycol	MEG
	propane 1,3 diol	PDO
	propylene glycol	PG
	hexamethylene diamine	HMD
	terephthalic acid	TPA
	tetrahydrofuran	THF
Polymers	acrylonitrile butadiene styrene	ABS
	expanded polystyrene	EPS
	polyamide	PA
	polybutylene succinate	PBS
	polybutylene adipate co-terephthalate	PBAT
	polybutylene terephthalate	PBT
	polycaprolactone	PCL
	polycarbonate	PC
	polyethylenes	PE
	· high density polyethylene	· HDPE
	· low density polyethylene	· LDPE
	· linear low density polyethylene	· LLDPE
	polyethylene furanoate	PEF
	polyethylene terephthalate	PET
	polyethylene isosorbide terephthalate	PEIT
	phenol formaldehyde	PF
	polyhydroxy alkanoates	PHA's
	polylactic acid	PLA
	polypropylene	PP
	polypropylene carbonate	PPC
	polystyrene	PS
	polytrimethylene terephthalate	PTT
	polyurethane	PU
	polyvinyl chloride	PVC
	polyvinyl alcohol	PVOH
	thermoplastic starch	TPS
	unsaturated polyester	UP
Compounded	bulk molding compound	BMC
	sheet molding compound	SMC

## Executive Summary

Key conclusions of this study include:

- (1) The bioplastics industry is a small but rapidly growing section of the overall 270 million tonnes plastics industry. Growth estimates for bioplastics from various market studies range from 19% to over 30% per year. In the opinion of Jim Lunt and Associates actual growth is closer to the 19% value based on a thorough evaluation of the actual volumes being sold as opposed to declared capacities.
- (2) First generation compostable bioplastics (polylactic acid (PLA) and compounded starch products still represent the major category of bioplastics and have captured market share from commodity thermoplastics such as polystyrene, polyvinyl chloride (PVC) and polyethylene terephthalate (PET) in primarily single-use disposable application segments. The polyolefin markets have not been penetrated by first generation compostable bioplastics due to their unique combination of low specific gravity, performance spectrum and pricing compared to these bioplastics.

Recently, other non-compostable thermoplastics such as bio polyethylene (PE) partially biobased polyesters such as PET and polybutylene terephthalate (PBT), polyamides and thermoset products such as polyurethanes (PU), epoxies, unsaturated polyesters (UP) and other bio plastics, are entering the marketplace as direct replacements for 100% oil based equivalents.

- (3) The bioplastics market has evolved considerably over the last 5 years with many performance deficiencies of the early compostable bioplastics having been overcome by the use of additives and compounded polymer blends. There are still opportunities to further improve performance but cost and commercialization times for completely new approaches may be prohibitive. Overall, for all bioplastics, pricing and performance against petrochemical-based plastics are still significant issues. Due to these concerns, recent commercialization activity in bioplastics has largely shifted to the manufacture of conventional monomers and existing oil-based plastics from renewable resource based alternatives. Bio based polyethylenes entered the marketplace in 2010 and have been successfully displacing their oil-based counterparts. However, the recent expansion in natural gas availability has led to concerns about the ability of the bio-based olefin analogues to compete on price with natural gas derived products.
- (4) Bio derived chemicals such as monoethylene glycol has enabled the commercialization of a 20% renewable carbon content PET by Coca Cola for their "Plant Bottle". As yet the bio aromatic component –terephthalic acid, has not been produced commercially although this is an area of intense development. In contrast to the polyethylene scenario, plentiful natural gas may actually accelerate activity in the bio-aromatics area since natural gas does not contain aromatics.
- (5) The last few years have seen a growing number of governments' worldwide developing strategies and policy frameworks to support the development of a sustainable and competitive bioeconomy. Several of these policies offer generic support for the further development of biochemicals, biomaterials and bioplastics, promoting bio-based products or the bio economy in general. Most of them focus on research and innovation. Many countries have implemented policies banning single use plastics bags. However, only a few countries have developed a specific set of policies targeting the development of bioplastics.
- (6) Pressure is increasing to replace food crops as feedstocks for bio plastics with agricultural or forestry biomass. Technology advancements are being made to cost effectively extract sugars from these waste products but as yet no commercial scale plant is operational. Some key players are emerging

as leaders in this area. Other key issues with biomass feedstocks, in addition to efficient extraction, are the logistics of supply, storage and accumulation of sufficient quantities for processing.

All of the above trends are discussed in the body of this report.

**SECTION 1. Present size and segmentation of the conventional plastics industry by volume of plastics used overall (not application by application).**

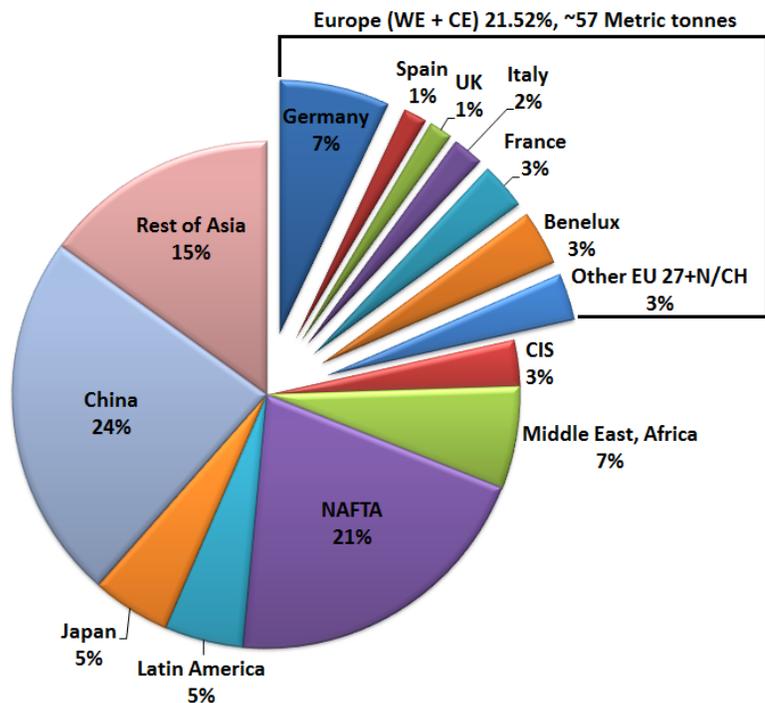
From 2009 to 2010 the global production of plastics increased by 15 million tonnes or 6% to 265 million tonnes<sup>1</sup>, confirming the long-term trend of plastics production growth of almost 5% per year over the past 20 years. Due to the global recession, plastics growth from 2010 to 2013 slowed significantly although plastics production is still estimated to have reached 270 million tonnes in 2014. In 2010 Europe accounted for 58 million tonnes (21.5%) of the global production, and China had surpassed Europe as the biggest production region at 23.5%. – Figure 1.

<sup>1</sup>[http://www.plasticseurope.org/documents/document/20111107101127--final\\_pe\\_factsfigures\\_uk2011\\_lr\\_041111.pdf](http://www.plasticseurope.org/documents/document/20111107101127--final_pe_factsfigures_uk2011_lr_041111.pdf)

Total plastics consumption is expected to continue at an average growth rate of 5% - 6%, and is projected to reach 297 million tonnes by 2015.

The conventional oil based plastics industry comprises thermoplastics and thermosets. Thermoplastics are generally defined as plastics which soften when heated. Thermosets in contrast are completely infusible and are generally made from two reactive components which harden or “cure” during the reaction. The thermoset resins market is approximately one third of the size of the thermoplastics market and is expected to reach 87.7 million tonnes by 2016.<sup>2</sup>

<sup>2</sup>[http://article.wn.com/view/2013/01/15/Research\\_and\\_Markets\\_Thermosets\\_Resin\\_A\\_Global\\_Market\\_Watch/](http://article.wn.com/view/2013/01/15/Research_and_Markets_Thermosets_Resin_A_Global_Market_Watch/)



**Figure 1. Global Production of Plastics by Region<sup>1</sup>.** Global production of plastic is ~265 metric tonne with Europe accounting for approximately 57 metric tonne. Figure modified from<sup>1</sup>.

**Thermoplastics**

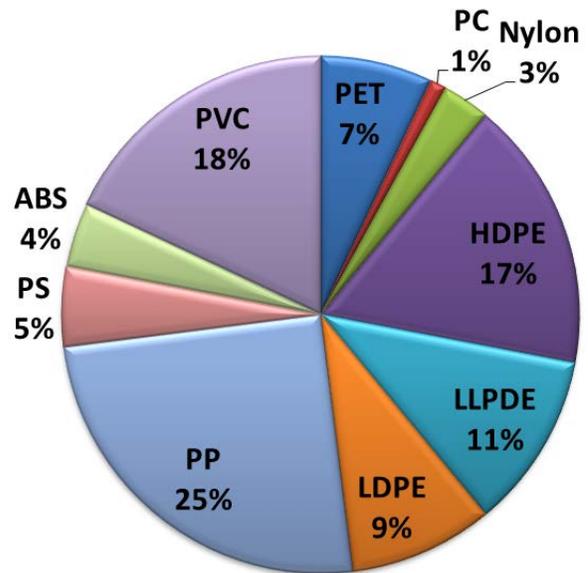
The thermoplastics industry is divided broadly into commodity and engineering plastics. Commodity plastics are generally characterized by low price and properties not suitable for durable, demanding applications without the use of additives, reinforcing fillers, fibers or polymer blends. Engineering plastics are much more robust in their properties and more expensive. Typically, they are used in niche and demanding applications in contrast to the large volume single-use markets occupied by commodity plastics.

Examples of commodity plastics are: polystyrene (PS), polyvinyl chloride (PVC), polypropylene (PP) and polyethylenes (PE). Typical market shares for these plastics are illustrated in Figure 2<sup>3</sup>. Clearly the polyolefins which comprise polypropylene (PP), linear low density polyethylene (LLDPE), low density polyethylene (LDPE) and high density polyethylene (HDPE) dominate this segment.

<sup>3</sup>Chase Willet CMAI-Presentation, Plastics Recycling Conf. 2011, LA, New Orleans 2011.

Commodity plastics account for approximately 80% of all thermoplastics. Major applications are in flexible films for bags and wrapping, cutlery, bottles, food trays and other single-use applications. Pricing for these materials are generally in the range \$1.32- \$3.3/kg.

Engineering thermoplastics are typified by materials such as polycarbonate (PC), polyethylene terephthalate (PET), polybutylene terephthalate (PBT) and a range of polyamides or nylons. Asia-Pacific is one of the dominant markets for engineering plastics, accounting for 38.3% of the global market in 2011. The major applications for engineering plastics include automotive and transportation, electrical and electronics, industrial and machinery, packaging, and appliances. Pricing for these materials is generally in the range \$3.30 to \$4.40/kg. For very high performance materials such as polyether ether ketone, polysulfone and polyimide, for example, which are used in aero space and other very demanding applications, prices can reach well over \$10/kg.



**Figure 2. Global Plastics Consumption by Type.** World polymer demand in 2010 was 196 million metric tons. Figure modified from<sup>3</sup>.

There is overlap in some commodity/engineering markets where commodity resins such as PP, ABS and engineering resins such as PET, can compete depending on the applications and level and type of modification required.

High performance plastics are the smallest segment of the industry but show the highest growth rate and command high prices. As we move down into more commodity materials the market expands with lower growth rates. As the market grows, pressure increases on price. Ultimately, based on performance within specific market sectors, price and volume begin to plateau.

### Thermosets

The global market for thermosets is expected to experience double digit growth from 2012 to 2016 reaching 105.3 million tonnes by 2016.<sup>4</sup> This is just over a third of the size of thermoplastics demand.  
<sup>4</sup><http://www.prnewswire.com/news-releases/thermosets-resin---a-global-market-watch-2011---2016-225791541.html>

Key thermoset materials include unsaturated polyesters (UP) and phenol-formaldehyde (PF) which together account for approximately 30% of the total global market. Other products include

polyurethanes (PU) and epoxy/polyepoxide resins. Key thermoset end use markets include plywood adhesives, furniture/bedding, building & construction, automotive, consumer products and electronics.

Geographical analysis<sup>5</sup> of the thermoset marketplace shows that the highest Compounded Annual Growth Rate (CAGR) of 11.7% is anticipated for the Asia-Pacific region during the period, 2011-2016  
<sup>5</sup><http://www.businesswire.com/news/home/20130115005697/en/Research-Markets-Thermosets-Resin---Global-Market#.U6Xb8UBgFEM>

The market for thermosets is dominated by big multinational corporations which are present across the value chain. Some of the major companies operating in the thermosets market include Arkema, BASF, Asahi Kasei Chemical Corp., Bayer AG, Chevron Phillips Chemical Company LLC, Sinopec, Dow Chemical Company, Eastman Chemical Company, and LyondellBasell Industries

The growing demand for thermosets from emerging economies like Brazil, Russia, India, and China (BRIC) is expected to drive the market. BRIC nations are the four fastest growing economies in the world with their GDP growth rates higher than the global GDP growth rate. However, frequent fluctuation in raw material prices acts as one of the major factors inhibiting the market growth.

Asia-Pacific presently accounts for the biggest market for thermosets owing to the growth of the automobile market primarily in China and India. Japan is a mature market and is expected to remain stagnant over the next six years. China is the biggest automobile market in the world and India also lists itself in the top five automobiles market in the world. Asia along with being the largest market is also the fastest growing market for thermosets.

The North American market for thermosets is primarily driven by the regulatory initiative to reduce automobile weight by 50% by 2020 in order to cut fuel consumption. Unsaturated polyester resins and polyurethanes account for the two biggest types of thermosets in this market followed by phenolic and epoxy resins.

## **SECTION 2. Volumes and key performance attributes of conventional oil-based plastics used in key attractive application segments for substitution by bioplastics.**

In 2009, European Bioplastics in partnership with the European Polysaccharide Network of Excellence (EPNOE) published a report by the University of Utrecht entitled “*Product overview and market projection of emerging bio-based plastics-PRO-BIP 2009*”. The conclusions of this report were that the total maximum *technical* substitution potential of bio-based polymers replacing their petrochemical counterparts was estimated at 90% of the total polymers being produced globally. The term “technical” was used to estimate what could be achieved if all issues associated with feedstock availability, technical feasibility, scale up economics and processing issues could be resolved. In reality, the actual conversion routes from sugars to conventional monomers for many polymers are unlikely to be practical, scalable or economic and so it is difficult to understand this assertion.

The report stated that such potential would not be realized in the medium term (i.e. by 2020). The main reasons cited were economic barriers (especially production costs and capital availability), technical challenges in scale-up, the short-term availability of bio-based feedstocks and the need for the plastics conversion sector to adapt to the new plastics. In another study published by the Nova-Institute GmbH<sup>6</sup> on March 06, 2013, it was projected that the production capacity for bio-based polymers will triple from 3.5 million tonnes in 2011 to nearly 12 million tonnes in 2020.

<sup>6</sup>Nova-Institute GmbH ([www.nova-institute.eu](http://www.nova-institute.eu)), Hürth, 6 March 2013

Neither of these studies, as well as many similar studies, has considered the various types of bioplastics and how their properties dictate where they will truly compete in specific markets and against which petroleum-based materials. Additionally, the recent developments in the availability of natural gas in the USA will impact many of their conclusions, specifically in the polyolefins sector.

The actual key attractive application segments for substitution by bioplastics depend on the type of bioplastic and its competitive attributes which will facilitate the replacement of a conventional plastic. Bioplastics are not just one single substance but comprise a whole family of materials with differing properties and applications.

### **Drivers for Bioplastics Adoption:**

In the 1980’s concerns over diminishing land fill space fueled interest in plastics that could be diverted from landfills and disposed of by alternative means. Of particular interest were biodegradable or compostable plastics since they were considered to have the potential to displace conventional non compostable plastics which were contaminated with food waste and could not easily be recycled. First generation plastics such as polylactic acid (PLA) and compounded starch products were developed to meet this need. Later questions were raised about the use and depletion of finite resources such as oil for both energy and plastics manufacture. Bioplastics terminology and products were widened to encompass renewable resources as alternative feedstocks to oil. Compostability was no longer the only driver. In the 1990’s global warming, stemming from green house gases became another issue. Life cycle analysis became common place to demonstrate that bioplastic manufacture, in many cases, is better from an energy, greenhouse gas and overall sustainability perspective than oil based products. The concept of biobased carbon was also introduced. Finally, increasing concerns about the effects on human health of monomer residues and additives in oil based plastics are being raised. Bioplastics in general have not yet been

shown to be an improvement over oil based plastics in this regard. However, as bioplastics move forward this issue will further steer the direction of bioplastics developments. The overall result of this increasing spectrum of concerns is that the bioplastics industry has broadened considerably from the early compostable plastics to encompass a wide variety of materials and technologies.

### **Bioplastic Definitions:**

There has been ongoing confusion as to what defines a bioplastic. According to European Bioplastics<sup>7</sup> a plastic material is defined as a bioplastic if it is either biobased, biodegradable, or features both properties. The schematic representation of bioplastics according to EU Bioplastics is shown in Figure 3.

<sup>7</sup>[http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Bioplastics\\_eng.pdf](http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Bioplastics_eng.pdf)

**Biobased plastic definition:** The term “biobased” means that the material or product is (partly) derived from biomass (plants). Feedstocks used for today’s bioplastics stem from corn, sugarcane, soy beans or cellulose. Biobased content is defined by the amount of renewable carbon and ranges from approximately 20% to 100%.

**Biodegradable plastic definition:** Biodegradation is a chemical process during which micro-organisms that are available in the environment convert materials into natural substances such as water, carbon dioxide, and compost. The process of speed of biodegradation depends on the surrounding environmental conditions (e.g. location or temperature), on the material and on the application.

The property of biodegradation does not depend on the resource basis of a material, but is rather linked to its chemical structure. In other words, 100 percent biobased plastics may be non-biodegradable, and 100 percent fossil based plastics can biodegrade.

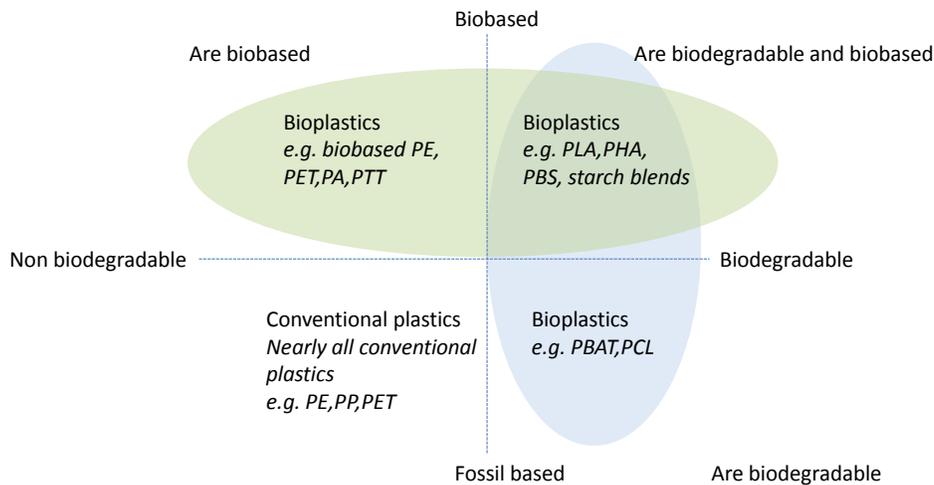
### **Classification of Bioplastics:**

Bioplastics are broadly divided into three main groups:

- (a) Plastics that are both biobased and biodegradable, for example, polylactic acid or polylactide (PLA), starch-based blends (TPS), cellulose acetates, polyhydroxy alkanooates (PHA’s) and potentially polybutylene succinate (PBS).
- (b) Biobased or partly biobased non-biodegradable commodity thermoplastics such as biobased PE, PP, PVC or PET (so-called drop-ins) and biobased technical performance polymers such as polytrimethylene terephthalate (PTT) and nylon 11 (based on amino undecanoic acid from castor oil) and other polyamides (PA). In addition there are biobased thermosets such as the soy-based polyurethanes, unsaturated polyesters and epoxies which should be included in this group.
- (c) Plastics that are presently based on fossil resources and are biodegradable. The most noteworthy of these are polybutylene adipate terephthalate (PBAT), PBS and Polycaprolactone.

These specific materials represent over 95% of the total activity in bioplastics and can be used to discuss trends in the industry, key attributes and projected attractive market segments of displacement.

Figure 3 depicts typical bioplastics and how they are classified by European Bioplastics<sup>7</sup> according to their biodegradability.



**Figure 3. Classification of Bioplastics Based on Biodegradability.** Figure modified from<sup>7</sup>.

Missing from specific mention in the European classification are the soy-based polyurethanes and other biobased thermosets such as epoxies and unsaturated polyesters which are entering the marketplace. This study will discuss developments in both the biobased thermoplastics and biobased thermoset sectors.

**(a) Plastics that are both biobased and biodegradable, such as PLA, PHA's, Cellulose Acetates and Thermoplastic Starches.**

In addition to historically known limited volume, naturally occurring biobased products such as albumen, chitin, amber, shellac, collagen keratin, ebonite, Zein and cellulotics, there is a new class of man-made products such as PLA, PHA's, and thermoplastic starches. Aliphatic polyesters such as polybutylene succinate, which conventionally are oil based, are also entering the marketplace based on renewable resource precursors. These new bioplastics can all be ultimately digested by microorganisms and converted anaerobically or aerobically back to simple compounds such as methane, carbon dioxide and water. PLA, which is produced from fermentation derived lactic acid, must first be broken down by hydrolysis before microorganisms will recognize it as a food source. A common attribute of all these materials is their ability to be disposed of in microbial rich environments such as municipal composting facilities or anaerobic waste digesters. While products such as PLA and PHA's are based on renewable resources such as corn sugar, others may also contain non renewable resource oil derived feedstocks or polymers such as in the starch blends with fully synthetic biodegradable polyesters such as Ecoflex (BASF trade name for PBAT), PBS and Polycaprolactone (PCL).

These biodegradable products represent the first generation of modern commercial bioplastics. Their ability to be digested by microorganisms has led to the initial targeting of non-biodegradable/compostable oil-based products used primarily in single-use disposable products. The primary driver for displacement of conventional oil-based plastics in these

segments was originally compostability but this has widened somewhat to include environmental, potential effects on human health, and overall sustainability features. Primary displacement targets are commodity thermoplastics such as polystyrene, PVC and some markets occupied by PET. Although claims are made that these materials can also displace polyolefins such as PP and HDPE the performance spectrum and pricing of these commodity plastics makes such displacement extremely difficult. Bioplastics in this class typically have specific gravities of 1.23 to 1.40 compared with 0.9 to 0.94 for the polyolefins. Assuming equivalent conversion efficiencies leads to a 20- 50% reduction in the number of parts that can be produced from bioplastics versus the polyolefins. For polystyrene, PVC and PET, biodegradable or compostable plastics can more readily displace segments occupied by these materials due a smaller difference in specific gravities and more similar performance.

### **Market size of conventional plastics being targeted by bio based compostable plastics:**

#### **Polystyrene**

Demand for polystyrene and expandable polystyrene (EPS) is increasing within developing countries such as China, India, Iran, Saudi Arabia and Brazil according to Global Business Intelligence Research.<sup>8</sup>

<sup>8</sup>.[plastemart.com](http://plastemart.com)

The polystyrene packaging and food serviceware industries represent potentially lucrative substitution markets for bio-based plastics such as Polylactic acid (PLA), Polyhydroxyalkanoates (PHA's) and polybutylene succinate (PBS). Specific target markets include the food-service industry in single-use applications such as rigid trays and containers, disposable eating utensils, foamed cups, plates, and bowls. World demand for foodservice disposables is projected to grow 5.4 percent per year to over \$53 billion in 2015.<sup>9</sup>

<sup>9</sup>[http://www.trnusa.com/index.php?option=com\\_content&view=article&id=179:world-demand-to-rise-through-2015-for-foodservice-disposables&catid=4:articles&Itemid=1](http://www.trnusa.com/index.php?option=com_content&view=article&id=179:world-demand-to-rise-through-2015-for-foodservice-disposables&catid=4:articles&Itemid=1)

In a recent report from RnRMarketResearch.com<sup>10</sup> the global biodegradable plastic packaging market is projected to grow at a cumulative average growth rate (CAGR) of 18.1% from 2013 to 2019 to reach a value of \$8 thousand million (billion). Due to increasing degree of consumer awareness, and general and contract manufacturing activities in Europe and North America, the developed geographies are expected to register maximum growth. Country wise, the U.S. is the top consumer of biodegradable packaging product. Europe is the second largest consumer with Sweden, Switzerland, United Kingdom and Germany, plus other E.U. countries driving the growth of biodegradable packaging.

<sup>10</sup><http://www.prweb.com/releases/biodegradable-packaging/market-2019-forecasts/prweb11796468.htm>

While food packaging takes the top position in the biodegradable packaging market, with more than 70% share by value of biodegradable plastic packaging and more than 40% share by value of biodegradable paper packaging, maximum growth in the future is expected to be from the beverage packaging application segment which is dominated by polyethylenes, PET and PVC. Polystyrene, while being a very versatile material is the subject of several concerns. Polystyrene foam (EPS) has been banned in many geographies due to litter issues. In the food serviceware industry, the single-use nature of the products and contamination with food lead to the

products ending up in landfills. There is no recycling infrastructure for polystyrene. Styrene monomer is regarded as a possible human carcinogen, although despite significant debate no real evidence exists to support this classification. Nevertheless, consumer perception is driving companies to find alternatives to polystyrene foam and food serviceware products.

## PVC

The polyvinyl chloride (PVC) market has struggled for several years and has remained challenging throughout 2014. However, Suspension-grade PVC (S-PVC) capacity is projected to increase by 6% during 2014, to 59 million tonnes/year according to IHS Chemical<sup>11</sup> as producers trim production to match still-sluggish demand, the average operating rate in 2014 will be about 64.8% globally. This is over a percentage point lower than in 2013. Worldwide PVC demand is anticipated to reach 40.2 million tonnes in 2014, with an annual growth rate of 4.15%, offset by persistent oversupply.

<sup>11</sup>[http://www.chemweek.com/lab/Outlook-2014-Looking-forward\\_57898.html](http://www.chemweek.com/lab/Outlook-2014-Looking-forward_57898.html)

In Western Europe, the PVC industry remains fragmented, but there are signs of consolidation. The region's largest producers, Ineos and SolVin (a joint venture between Solvay and BASF) aim to complete plans to merge their PVC businesses. According to IHS the S-PVC capacities of Ineos and SolVin are about 1.8 million tonnes/year and 1.2 million tonnes/year, respectively. Elsewhere, North America's PVC exports will grow due to the region's improved cost position, and the Mideast will remain a significant exporter in 2014.

The primary market segments for PVC are in extruded profiles, pipes and fittings and flexible films. In these segments typical PVC applications include:

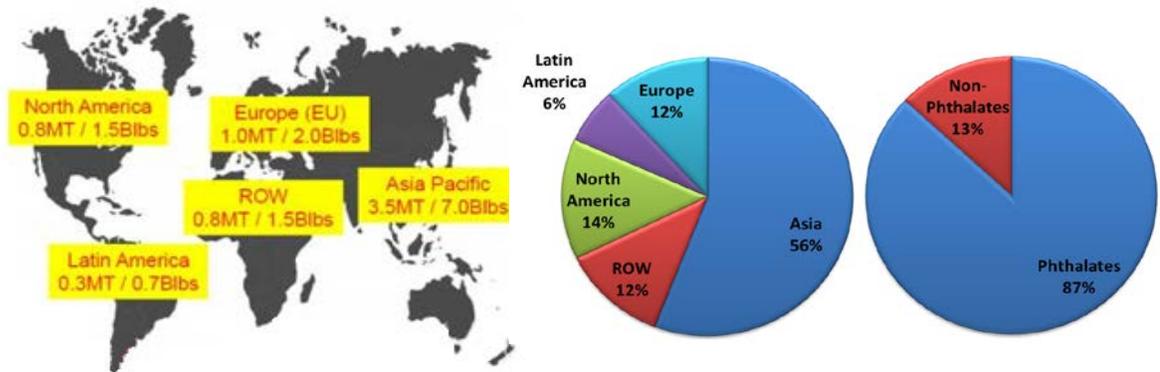
1. Water pipes, tubing, hoses.
2. Wire and cable insulation.
3. Wallpapers.
4. Clear folders.
5. Window/door profiles or sidings.
6. Synthetic leather cloth (for furniture upholstery, diary covers).
7. Laminates (gypsum boards or speaker boxes).
8. Clothing.
9. Toys.
10. Inflatables - pool toys, waterbeds.

The key attributes of PVC which drive its applications include:

1. Inexpensive (\$2.07-\$2.60/kg depending on grade)
2. Inherent fire retardant properties (reduced by addition of plasticizers).
3. Wide property spectrum - From highly rigid to very flexible by the use of a variety of plasticizers.
4. Durable under a wide variety of conditions.

Substitution of PVC by bioplastics is difficult due to its wide property spectrum and price. Some limited penetration has been made in the sheet market for gift cards which represents less than

5 % of all PVC use. The real major opportunities for bioplastics in PVC lie in displacing the phthalate plasticizers. As shown in Figure 4, in 2011, 95% of all plasticizer use was in PVC of which 87% were phthalates of various types.



**Figure 4. Regional demand for plasticizers.** World plasticizer consumption in 2011 was ~6.4MT/14 billion lbs with ~95% of plasticizers used in flexible PVC. Overall the trend is for steady global growth driven by emerging economies. Rest of world (ROW), figure modified from<sup>12</sup>.

### Polyethylene Terephthalate

While PET is not traditionally considered a commodity plastic it does compete against polystyrene and PVC in many markets.<sup>13</sup> Figure 5 illustrates the total demand and market segments for PET in 2011. <sup>13</sup>Chase Willet CMAI-Presentation, Plastics Recycling Conf. 2011, LA, New Orleans 2011.

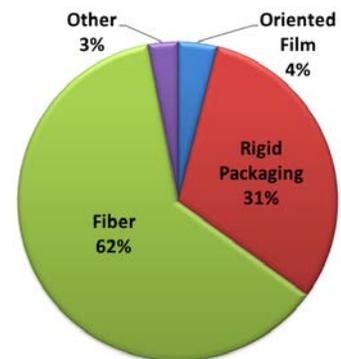
According to a recent Research and Markets<sup>14</sup> report, Polyethylene Terephthalate (PET) volume is expected to reach 69 million tonnes by 2016 primarily by growth in - Films, Fibers and Sheet Extrusion markets.

<sup>14</sup><http://www.reuters.com/article/2013/02/19/research-and-markets/idUSnBw6K24gxa+120+BSW20130219>

Bottles, containers and food packaging segments presently account for approximately 62.6% of the PET market share. Geographical analysis shows that the highest CAGR of 11.7% is anticipated to be in Europe over the period 2011-2016. Asia-Pacific follows Europe with a CAGR of 11.3%. The Americas is projected to show a CAGR of 10.9%.

The key attributes of PET in these sectors are:

- High clarity and gloss.
- Ability to crystallize in orientation process such as injection stretch blow molding and biaxial orientated films.
- Low water vapor transmission, carbon dioxide and oxygen transmission compared to polyolefins.



**Figure 5. Polyethylene Terephthalate End Uses.** 2011 total demand 30.9 million metric tons. Figure modified from<sup>13</sup>.

- Recyclability.

Starch-based products, cellulose and PHA's presently do not compete against PET except for limited penetration by cellulose into PET films. PLA does not readily compete with PET in the bottle market because of poor barrier properties and concerns about contamination of the PET recycle stream. PLA is displacing PET in single-use thermoforming applications with an addressable market of around 7% of all PET packaging, or just more than 1million tonnes globally, according to UK-based consultancy Smithers Pira.<sup>15</sup> PLA is also being used in fibers primarily for wet wipes applications.

<sup>15</sup><https://www.smitherspira.com/market-reports/emerging-regions-to-drive-growth-in-pet-packaging-consumption-to-2015.aspx>

- (b) Biobased or partly biobased non-biodegradable thermoplastics such as biobased PE, PP, PVC or PET (so-called drop-ins) and biobased technical performance polymers such as PTT. Biobased thermosets such as the soy-based polyurethanes unsaturated polyesters and epoxies.**

### **Bio Polyolefins**

In 2010, the introduction of a 100% biobased equivalent to HDPE by Braskem revolutionized the bioplastics industry in that for the first time the driver was not compostability but renewable resource content. Derived from sugar cane ethanol this product is chemically equivalent to its petroleum based counterpart and so can be used in the same markets. Braskem presently claims to have a 200,000 tonnes capacity in Brazil.

In February last year<sup>16</sup> Braskem announced it will not be pursuing its "Green PP" initiative and will also not be putting any more effort into bioethylene. Dow Chemical and Mitsui have also delayed their US \$1.5bn project to produce PE from sugarcane in Brazil<sup>17</sup>. In these projects, ethanol would be produced from sugarcane and then used to produce 900,000 tonnes/ year of various grades of PE. The projects would have been the world's largest biopolymers investments. Apparently this change is in response to concerns around the economics of these products and the increasing availability of cheap shale gas in the USA.

<sup>16</sup><http://www.bnamericas.com/news/petrochemicals/braskem-freezes-green-plastics-plans-focuses-elsewhere>

<sup>17</sup><http://www.plasticsnews.com/article/20130110/NEWS/301109988/dow-and-mitsui-postpone-sugarcane-polymer-plant>

These recent announcements are likely to delay and potentially reverse any near term penetration of the polyolefins industry by their biobased analogues and have significantly changed the growth projections for bioplastics as a whole.

### **Bio PVC**

PVC can be produced completely from renewable resources. As early as 2007, Solvay Indupa, the Brazilian arm of Belgium-based chemical giant Solvay, announced plans to use Brazilian sugarcane ethanol as a PVC feedstock. The chlorine component of PVC already comes from brine. The decision whether or not to proceed remains in the project stage, but a plant of 120,000 tonnes a year was envisioned. However, economics are uncertain, especially given the

recent announcements by Braskem around bio polyethylene costs. In addition, concerns around dioxins produced during incineration of PVC and the carcinogenic nature of vinyl chloride monomer will not be alleviated by the use of renewable resources.

### **Bio PET**

Today, Bio PET has only the glycol component derived from sugar cane ethanol and so the product has 20% renewable carbon content. The primary markets for this product are bottles (Coca Cola), Pantene shampoo packaging (Proctor & Gamble) and Ketchup bottles (Heinz). Total capacity today is approx. 700,000 tonnes/year. Capacity is projected to grow to 5 million tonnes by 2017.<sup>18</sup>

<sup>18</sup>[http://en.european-bioplastics.org/wp-content/uploads/2013/publications/EuBP\\_FS\\_Rigid%20Packaing\\_March2013.pdf](http://en.european-bioplastics.org/wp-content/uploads/2013/publications/EuBP_FS_Rigid%20Packaing_March2013.pdf)

Bio PET is chemically identical to 100% petrochemical based PET and so in principle can be used to displace conventional PET across all market segments. However, the cost of bio ethylene glycol is still considerably higher than its petro based equivalent, and so market penetration will be restricted. As with bio PE, the competitiveness of bio ethylene glycol will be affected by the shale gas supply of cheap ethane. Under the sponsorship of Coca Cola companies are also working to produce a bio derived terephthalic acid (TPA) but as yet commercial success is not guaranteed.

### **Bio PTT**

Similar to bio PET, PTT has only the glycol component –propane 1,3 diol (PDO), derived from a renewable resource. PTT's biobased carbon content is 28%. PTT is produced by DuPont and marketed under the trade name Sorona™. Primary target markets are to displace nylon 6 and 6, 6 in the carpet industry and for use in apparel and automotive fabrics.

Key claimed performance properties include:

- Production of Sorona® uses 30% less energy and reduces CO2 emissions by 63% compared to the production of an equal amount of nylon 6. When compared to an equal amount of nylon 6,6 production of Sorona® uses 40% less energy and reduces greenhouse gas emissions by 57%.
- Extraordinary softness.
- Exceptional comfort stretch.
- Brilliant color and easy care.

DuPont has around 63,500 tonnes/year Bio-PDO capacity in Loudon, Tennessee. This is equivalent to approximately 170,000 tonnes of PTT.

In March 2013, France-based Metabolix Explorer announced that the company and its partner Malaysian biotech hub owner Bio-XCell are pushing ahead for their plans to construct a 50,000 tonnes/year biobased PDO facility in Bio-XCell's site in Iskandar<sup>19</sup>. The facility is expected to have an initial output of 8,000 tonnes/year, using crude glycerol as feedstock. When fully operational this facility could produce up to 140,000 tonnes/year of PTT.

<sup>19</sup><http://greenchemicalsblog.com/2013/03/18/bio-pdo-market-update/>

## Bio Polyamides

Nylon 6 and 6,6 were introduced to the market in the 1940s as the first synthetic fibers. From the 1950s onwards, nylon demand for injection molding and extrusion grades has steadily grown accounting for 38 percent of the global demand for nylon today. Over time other types of nylons or polyamides have been introduced but today approximately 85-90 percent of polyamides in the global market are nylon 6 and nylon 6,6. The estimated total market for these two nylons in 2009 was 7.4 million tonnes.<sup>20</sup>

<sup>20</sup>[http://www.chemsystems.com/about/cs/news/items/PERP%200708S6\\_Nylon%206.cfm](http://www.chemsystems.com/about/cs/news/items/PERP%200708S6_Nylon%206.cfm)

China is the world's largest producer of nylon 6, representing 32% of the total world capacity. Overall global growth in nylon 6 capacity is driven by China's increasing demand and its desire to be more self-sufficient. Capacity additions are aggressive in China, and as a result, total global nylon 6 capacity (including nylon polymerization) is expected to grow at an 18.5% rate from 2012. The United States is the world's largest producer of nylon 6,6, accounting for 41% of the total world capacity<sup>21</sup>. Total world capacity for nylon 6,6 is expected to increase by 10% from the capacity level in 2012.

<sup>21</sup><http://chemical.ihs.com/CEH/Public/Reports/580.0800>

Although biobased nylon 6 and nylon 6,6 are not presently commercially available, Rennovia has announced their technology to produce both adipic acid and hexamethylene diamine monomers to enable bio nylon 6 and nylon 6,6.<sup>22</sup>

<sup>22</sup><http://www.rennovia.com/LinkClick.aspx?fileticket=SbQO8hcNOW8%3D&tabid=62>

In the presentation given by Rennovia in 2013, the market for nylon 6,6 in fibers was said to be 925 thousand tonnes/ year with a projected 2.3 % CAGR to 2022.

Nylon 6 has somewhat lower heat resistance than nylon 6,6 but has advantages in aesthetics (especially in reinforced compounds), easier color ability and historically lower cost. In practice, there is significant overlap in the performance of these two major nylon types. While the preference for 6 versus 6,6 varies by region, nylon 6 continues to hold the largest volume share of engineering plastic nylon resin globally by virtue of its broad use in the production of film used in packaging.

Automotive and truck applications are the demand drivers for both nylon 6 and 6,6 in all global regions, accounting for about 36% of global nylon resins consumption in 2012. Demand for nylon resins for these applications is forecast to grow at an average annual rate of 4.6% during 2013–2018.

Electrical and electronic applications account for about 12% of the global demand for nylon resins. The average annual growth rate for nylon resin consumption in electrical and electronic applications is forecast to be about 6.6% during 2013–2018. Consumption of nylon 6 will grow at about 7.4% while consumption of nylon 6,6 will grow at 5.9% per year.

The appliances market for nylons is fairly large and is growing. These applications account for about 8% of the global demand for nylon resins. The average annual consumption growth rate for nylon resins in appliances will be about 6.7% during 2013–2018.

Total world consumption of these nylon engineering resins is forecast to increase at an average annual rate of 4.4%. Good growth is projected in major markets such as automotive parts, electrical/electronics and appliances, and consumer products.

### **Thermosets**

The global market for thermosets is expected to experience double digit growth from 2012 to 2016 reaching 105.3 million tonnes by 2016.<sup>4</sup>

The largest sector is thermoset polyurethanes. The polyurethane market is expected to reach 16.3 million tonnes by 2016.<sup>23</sup>

<sup>23</sup>. <http://prezi.com/ikxthz2fdcqj/recycling-of-thermoset-polyurethane-foams/>

Over 75% of the global consumption of PU products is in the foams for construction, furniture, bedding, and automotive markets. Only the polyol component of the urethane is available for replacement by renewable products. Due to functionality differences it has not yet proven possible to displace more than 40% of the total polyol in the polyurethane. In addition to polyurethanes, unsaturated polyester resins and polyurethanes account for the two biggest types of thermosets used in the automotive industry followed by phenolic and epoxy resins. Unsaturated polyesters and epoxies with biobased content are appearing in the market due to the ready availability of bio propylene glycol and glycerol as byproducts of bio diesel production.

### **(c) Plastics that are presently based on fossil resources and are biodegradable.**

The most noteworthy of these is polybutylene adipate terephthalate or PBAT. PBAT today is produced completely from petroleum based resources although initiatives are already underway to produce a biobased analogue. The major supplier is BASF who markets the product under the Ecoflex™ brand name. There are also other minor suppliers in Korea. Ecoflex is said to be a statistical copolymer of butylene adipate and butylene terephthalate.<sup>24</sup>

<sup>24</sup>. [ECOFLEX Presentation by BASF](#)

The use of Ecoflex in the bioplastics industry is driven by its compostability and the unique flexible film properties it possesses. Ecoflex is typically blended with PLA to produce a product trademarked by BASF as Ecovio™. In late 2011 BASF expanded its Ecoflex® production in Ludwigshafen from 14,000 tonnes to 74,000 tonnes. BASF purchases PLA from NatureWorks LLC to produce Ecovio®. The major markets for Ecovio are compostable films for food wrap and lawn and leaf bags. Pricing for the compounded product is not known but PLA pricing is around \$1.98/kg for large customers and Ecoflex pricing is around \$5.41/kg. The volumes of Ecovio being consumed have not been disclosed. On a cost/ performance basis Ecovio does not compete against polyolefins so its primary markets are those where some form of legislation is the driver.

### **Overall conclusions on substitution of oil-based plastics:**

In the preceding discussion, projected volumes beyond 2020 for substitution of conventional plastics are given as high as 90% of a 270 million tonnes global market in 2014– which is also projected to continue at an average growth rate of 5% - 6% for the foreseeable future.

However, today this scale of replacement is clearly not achievable due to capacities, economics, performance and applications needs across a wide spectrum of sectors and geographies. If one looks at the major bio materials that are available today and their performance and application spectrum against specific incumbents, together with the changing dynamics of the plastics industry, then the projected total market volumes, application segments and issues can be broken down as illustrated in the Table 1.<sup>25</sup>

<sup>25</sup>J. Lunt & Associates, LLC.

**Table 1. Projected Market Potential for Bioplastics by Applications<sup>25</sup>**

Oil-based Incumbent	Bio-product	Application	Attributes	2014 Volume (million tonne)	Key Issues to Displace Incumbent
HDPE	100% bio HDPE	All existing HDPE apps.	Flexible, tough, easy processing. Low Density	45.9	Price, shale gas. Capacity
LDPE	100% bio LDPE	All existing LDPE apps	Flexible, tough, easy processing. Low density	24.3	Price, shale gas. Capacity
LDPE	Ecovio	Translucent films and lawn and leaf bags.	Good tear resistance can run on LDPE blown film	-	Price, capacity
LLDPE	89% bio LLDPE	All existing LLDPE apps.	Flexible, tough, easy processing. Low density	29.7	Price, shale gas, capacity
PP	Bio PP	All existing PP apps.		67.5	Price, Shale gas.
PS	PLA, PHA, starch blends	Single use Food service ware	Clarity, ease of processing, grease resistance	9.2 (68% of PS demand)	Tg 98C, price, clarity
PVC	Bio PVC	All existing applications	Price, range of properties, fire retardant	48.6	Price, Bio PVC does not address toxicity concerns.
PVC	PLA, PHA, Starch blends	Gift/Credit cards	Flexibility/printability, durability	2.4	Durability, Price.
PVC plasticizers	Soy polyols, citrate esters, PHA's	All flexible PVC apps.	Non migration, wide temperature range, durability	5.3	Price, durability, performance
PET	Bio PET	All existing applications	Clarity, barrier, recyclability	18.9	Price. shale gas
PET	PLA,PHA	Single use thermoforms/ fibers	Clarity, 65C Tg. Ease of processing, barrier properties.	1.3	Barrier, Tg.
					Clarity for PHA.
Polyurethanes, unsaturated polyester,	Soy polyols, propylene glycol, glycerol	Adhesives/ foams	Flexible foams, rigid durable products.	100	Price and performance vs existing products

\* Typical average biobased content does not exceed 10% of the final products.

**SECTION 3. The present state-of-the-art in terms of developing renewable resource based materials.**

- **Property deficiencies against oil-based incumbents.**
- **Issues and potential routes to cost-effectively and practically overcome these deficiencies.**
- **Routes considered are those being developed today and suggestions for alternative approaches.**

Given the diversity of bioplastics this is a large section and is probably best addressed by breaking down bioplastics into the following classifications:

**A. New polymers containing renewable resource “building blocks.”**

Examples in this class include: PLA, PHA’s, and PBS, Polyketals, PPC, Furanics, PTT, TPS, nylon 11, and other castor oil biobased polyamides.

**B. Conventional polymers developed either partially or completely from renewable sources.**

Examples include: Regenerated cellulose, cellulose acetate, starch blends, PET, PE, PP, PVC, polyurethanes, epoxies and unsaturated polyesters.

**C. New/existing renewable “building blocks” or monomers/oligomers for new and existing polymers.**

Examples include: Furan dicarboxylic acid (FDCA), adipic acid, hexamethylene diamine (HMD), glucaric acid, succinic acid, ethylene glycol, butane diol, Propane 1,3 diol, caprolactam, terephthalic acid, isosorbide.

**A. New polymers containing renewable resource “building blocks.”**

The term “New Polymers” is used in the context that these products are generally based on known technologies, which were once considered none commercially viable i.e. PLA from lactic acid. Poly (hydroxyalkanoates) or PHA’s from sugars, starch based blends, TPS, polypropylene carbonate, PTT and furanics. The key differentiator from “conventional plastics” is that these materials are typically new to the plastics industry as the industry attempts to move away from petroleum as the key resource and reduce their environmental footprint or become more “sustainable”.

A notable exception to the above classification is nylon 11 which is derived from castor oil and has been in commercial use since the 1950’s but is now being recognized for its renewable origin. Other new polyamides such as nylons 6,10, 10,10, and 10,12, all partially based on castor oil, are now emerging. Polybutylene succinate or PBS is included here since although it has been available for some time; its production from renewable resources is just becoming viable.

Completely new polymer chemistries are very rare. Typically the novelty lies in the path to producing the basic polymer building blocks or monomers from a renewable resource. This will be discussed later in Section 3.

**Product functional performance limits:**

**A.1 Aliphatic polyesters (PLA, PBS, PHA's)**

The known issues associated with the aliphatic polyesters such as PLA, PBS and PHA's are illustrated in Figure 6 below.<sup>26</sup>

<sup>26</sup>.Jim Lunt & Associates, LLC

Since PLA is the dominant material in the marketplace for this class of polyesters, there is significant information, both in academic and industry publications, available as to its performance issues, solutions proposed and other potential approaches that could be used. In some cases these same technologies could be applied to the other aliphatic polyesters. There is a wealth of research on the use of fillers, nucleating agents, polymer blends, copolymers and chemical modification strategies to overcome the various issues associated with PLA. It is not the intention of this report to cover all the work in the literature. In reality technologies which have been adopted commercially to date for PLA have been done so for specific reasons. PLA is the largest of the first generation bioplastics, its initial and still major targets are for single use compostable applications. These markets are driven by commodity pricing and typically require food approval. Only those technologies which are considered cost effective are simple to implement on existing equipment and have full food contact approval, have entered the marketplace. Focus in this section is on these approaches. New approaches are discussed if, in the author's opinion, they show the potential to become commercial within 5 years.

**Figure 6. Performance issues with first generation compostable bio-aliphatic polyesters.** Figure modified from<sup>26</sup>.

PBS	PLA	PHA
Hydrolytic Stability	Hydrolytic Stability	Hydrolytic Stability
Vapor Transmission	Vapor Transmission	Processability
Shelf Life	Shelf Life	Shelf Life
Tear Strength	Tear Strength	Economics
Food Approval	Melt Strength	Melt Strength
Distortion Temperature	Impact Strength	Impact Strength
	Distortion Temperature (amorphous)	

An article from *Plastics Technology*<sup>27</sup> gives a good general overview of technologies being applied commercially to overcome the deficiencies of first generation bioplastics.

<sup>27</sup><http://www.ptonline.com/articles/enhancing-biopolymers-additives-are-needed-for-toughness-heat-resistance-processability>

### Hydrolytic stability

Potential hydrolytic breakdown during use and melt processing and attempts to mitigate this is a key issue for compostable bioplastics such as PLA, PHA's, and PBS.<sup>28</sup>

<sup>28</sup>Improvement of thermal stability, rheological and mechanical properties of PLA, PBAT and their blends by reactive extrusion with functionalized epoxy. Polymer Degradation and Stability, Volume 97, Issue 10, October 2012, Pages 1898–1914.

In single-use, short-shelf-life applications, which are the primary target markets, hydrolysis during storage and use is not a major concern and is mitigated by controlling humidity during storage of the polymer before processing and also during storage of the final converted product. For longer use applications such as electronics and automotive use, hydrolytic breakdown in the application environment significantly restricts their use in these markets.

All three products require drying before packaging. These materials are aliphatic polyesters and like all polyesters, are subject to hydrolytic degradation. The rate of hydrolysis is dependent on temperature and moisture content. Although the products should be dried by the manufacturer to less than 400ppm and supplied in foil lined bags, cartons, or railcars, it is highly recommended these materials be further dried to less than 250 ppm before melt processing.<sup>29</sup>

<sup>29</sup><http://www.plasticstoday.com/mpw/articles/polylactic-acid-handling-drying-and-reclaim-considerations-pla>

Hydrolysis during melt processing leads to significant loss in molecular weight and subsequent poor mechanical properties. In common with aromatic polyesters, these products are susceptible to hydrolytic degradation during melt processing. The absence of aromatic groups also leads to elevated sensitivity to such breakdown.

Typically, when possible, the pellets are pre-crystallized to allow higher temperature drying. Most drying is done in dehumidifying hoppers using hot air at a very low dew point. The dehumidified air passes through a bed of pellets to extract moisture from the resin. A desiccant material, such as silica, absorbs moisture from the circulating air. Dual desiccant bed systems are common, in which one bed is on-stream while the stand-by bed is being regenerated. Either a time cycle or a predetermined decrease in air dew point is used to shift airflow from one bed to the other. The crystallized pellets can be dried at 65 – 90°C (150 - 190°F), using dehumidified air with a dew point of –40°C (-40°F). Higher drying temperatures can lead to softening and blocking of polymer in the dryer. Lower drying temperatures will result in extended drying times. Specific non crystalline grades of PLA with high D isomer content, which are typically supplied for adhesive layer or amorphous foams, cannot be crystallized prior to shipping or use. For these materials drying at much lower temperatures is required. Typical drying temperatures of 43-55°C (110 - 130°F) are recommended to prevent sticking in the dryer.

Although processors of PET or Nylons typically have drying capabilities but they may not operate accurately at these lower drying temperatures. Also processors of PP, PE and

polystyrene do not use dryers. For these latter processors this can be a significant capital investment to process these compostable polyesters.

### Heat Distortion Temperature (HDT)

PLA has a low heat distortion temperature of approx. 54<sup>0</sup> C. This limits the use of amorphous PLA to non load bearing applications and usage below 54<sup>0</sup> C. If fully crystalline, this performance ceiling can be raised to as high as 130<sup>0</sup> C and even higher for stereocomplex products.<sup>30</sup> However, achieving sufficient crystallinity to raise the HDT during conversion processes outside of fibers and biax films, has proved problematic even with the recent introduction of the new >95% L grades of PLA by NatureWorks LLC.

<sup>30</sup>Effect of a Nucleating Agent on Crystallization Behavior and Mechanical property of PLA stereocomplex. B.U. Nam<sup>1</sup>, B.S. Lee<sup>1</sup>, M.H. Kim,<sup>1</sup> and C.H. Hong<sup>2</sup>  
Korea University of Technology and Education (KUT),<sup>1</sup> Hyundai-Kia Motors Co., Ltd.<sup>2</sup>

To overcome the low temperature performance of PLA in typical thermoforming and injection molding applications, significant effort has been expended on accelerating the crystallization kinetics by the use of nucleating agents. Early studies focused on the use of inorganic materials such as talc. High loadings of talc of up to 10% by weight can significantly increase the crystallization kinetics of PLA. However, the speed of crystallinity is still typically too slow for conventional single step thermoforming or injection molding of thin parts and the resultant products are opaque. Talc filled PLA can be successfully thermoformed using a 2 step thermoforming process similar to that used in crystalline PET (CPET) products for bakery goods. However, the economics of this process do not lend themselves to being competitive with the standard one mold thermoforming process used for transparent polystyrene and PET articles.

More recently, an improved nucleating agent for PLA was found. This is an organic wax known as ethylene bis stearamide (EBS).<sup>31</sup> At loadings as low as 0.4% the kinetics of crystallization are dramatically increased and the product is translucent as opposed to opaque.<sup>31</sup>

<sup>31</sup>US. Patent Application Publication, US 2009/0311511A1. Published Dec. 17, 2009.  
Mitsui Chemicals, Inc.

The most recent advances in achieving higher heat distortion performance involve the use of higher L (95% or higher) PLA grades with a nucleating agent.<sup>32</sup>

<sup>32</sup><http://www.natureworksllc.com/Technical-Resources/High-Performance-Grades>

In spite of these advances, a high heat crystalline PLA product has not yet successfully been produced under conventional conditions other than in fibers and orientated film. Recent work on using heated molds during injection molding has been reported to provide heat resistant parts but little is actually known about the total cycle time or overall process economics. Heating the injection molding cavities to >60C as proposed by NatureWorks LLC is, in the opinion of Jim Lunt & Associates LLC., not practical on the multi cavity molds used commercially.

Another approach to improving the heat resistance of PLA is the use of stereo complex technology.<sup>33</sup>

<sup>33</sup><http://www.purac.com/EN/Bioplastics/PLA-applications/High-heat-packaging.aspx>

Lactic acid exists in two enantiomeric forms the D and L form. Typical grades of PLA produced today consist primarily of the L form. However, technology is known and available to make the D form of lactic acid which can then be used to produce the primarily D form of the polymer. By melt blending a high L grade of PLA (> 98%L) with a high D form of PLA (> 98%D) - upon processing and cooling a stereo complex is formed. Surprisingly although the individual forms of PLA both have melting points of around 175<sup>0</sup>C the stereo complex can show a melting point in excess of 230<sup>0</sup>C. However, this technology appears to only work effectively in processes involving orientation such as biaxially orientated film or fibers. For the orientated film other than higher melting point and possibly lower shrinkage no other mechanical or gas transmission properties appear to be improved.

Another approach considered to resolve the heat performance of PLA while retaining compostability and renewable resource origin was by producing polymer blends. Some limited work was done by Tianan Biologic in China where they produced blends of PHBV and PLA.<sup>34</sup>

<sup>34</sup><http://www.innovationtakesroot.com/more-itr/itr-2010/itr-2010-conference-report>

Significant improvement in heat deformation was claimed with a 30% loading of PHBV as shown in Table 2.

However, no actual real life data on finished parts has been presented. In addition, the cost of PHBV and its lack of food approval severely restrict the utility of this approach.

Blends of PLA with petrochemical non compostable petroleum based polymers have also been studied and introduced to the marketplace by RTP.<sup>35</sup>

<sup>35</sup><http://www.rtpcompany.com/news/press/bioplastics.htm>

**Table 2. Heat distortion temperatures of PLA / PHBV blends at 0.45 MPa load.** Figure modified from<sup>34</sup>.

Sample	HDT (Celsius)
100% PLA	52
90% PLA / 10% PHBV	53.4
80/20	54.5
70/30	54.6
60/40	63
50/50	66.3

Typical claimed performance for some of their PLA compounds are shown in Table 3.

**Table 3. Comparison of PLA blends.** Table modified from<sup>35</sup>.

Polymer (% PLA)	Test (units)					
	S.G. - ASTM D792	Notched Izod - ASTM D256 (J/M)	Tens. Stren. - ASTM D638 (Mpa)	Tens. Elong. - ASTM D638 (%)	Flex. Stren. - ASTM D790 (Mpa)	Flex. Mod. - ASTM D790 (Gpa)
PLA (100)	1.24	13	53	6	83	3.8
PLA/PC (32)	1.18	881	48	10	83	2.4
PC (0)	0.95	961	61	>10	-	2.4
PLA/ABS (40)	1.12	294	54	>10	83	2.5
ABS (0)	1.1	507	113	56	-	3.1
PLA/PMMA (40)	1.21	37	69	6	121	3.8
PMMA (0)	1.1	107	85	85	143	3.6

In 2010, Arkema introduced its Plexiglas Rnew (TM) products based on Acrylic/ PLA alloys having >25% bio-renewable content.<sup>36</sup>

<sup>36</sup><http://www.plexiglas.com/en/media/news/news/Plexiglas-Rnew-Bio-based-Acrylic-Resins-from-Arkema/?back=true>

These alloys are targeted at durable application in consumer, medical, optical and automotive markets. PMMA and PLA are completely miscible in all proportions which results in transparent products with higher HDT than PLA. Typical properties are shown in Table 4.<sup>37</sup>

<sup>37</sup>[http://www.innovationtakesroot.com/~media/ITR2012/2012/presentations/durables/03\\_Plexiglas-RNew-Acrylic\\_Barsotti\\_pdf.pdf](http://www.innovationtakesroot.com/~media/ITR2012/2012/presentations/durables/03_Plexiglas-RNew-Acrylic_Barsotti_pdf.pdf).

Concerns around these blends, in the author's opinion, include durability due either to moisture penetration or the presence of lactide generated by the higher temperature compounding conditions. Disposal of these compounded products could also be an issue. The only driver for these blends appears to be biobased content and not increased performance of the base polymer.

**Table 4. Plexiglas® RNew Acrylic/PLA Alloys.** Table modified from<sup>37</sup>.

Property	Traditional Acrylic	30% Renewable Carbon
Melt Flow (230°C / 3.8 kg)	1.6	4.6
Nothced Izod (ft lb/in)	0.44	0.5
Tensile Modulus (kpsi)	500	499
Tensile Stress at Yield (psi)	10400	10700
Elongation at Break (%)	8.8	14.6
Rockwell Hardness (M)	92	85
Vicat (10N, 50°C/hr)	103	88
Optical Transmission	92	92
Haze	<2	4

For PBS its melting point is around 110°C and its glass transition temperature is very low at -44°C. Pure PBS uses will likely be limited by these properties. Blends of PLA and PBS have been proposed and in fact introduced in the marketplace by Amberworks (Bioamber and NatureWorks LLC.).<sup>38</sup>

<sup>38</sup><http://www.icis.com/resources/news/2012/02/16/9533080/bioplastics-jv-amberworks-to-sell-resins-at-2-2-50-lb/>

These blends were proposed for brittleness reduction of PLA and for flexible films. However, lack of food approval for PBS and pricing of around \$5.50/kg has limited the commercial utility of such blends.

Poly Hydroxy Alkanoates (PHA's) represent an emerging class of biopolymers which are presently produced through the fermentation of natural sugars and, potentially, vegetable oils or fatty acids. These materials are unique in the field of renewable resource based biopolymers in that they represent the only class of polymers which are converted directly by microorganisms from feedstock to the polymeric form - no additional polymerization steps being required. The product, in the form of microscopic granulates, is extracted from the microbial cells and used either as the powder or converted to pellets for ease of shipping and handling. Also, during the melt conversion to pellets, additives such as an antioxidant and nucleating agent to accelerate crystallization can be incorporated.

Interest in PHA's has spanned many decades<sup>39</sup>. Today there are actually over 300 known microorganisms capable of producing PHA's and over 150 monomer combinations that can produce PHA's with widely different properties.

<sup>39</sup>. Biotechnological approaches for the production of Polyhydroxyalkanoates in microorganisms and plants — A review. *Biotechnology Advances* 25 (2007) 148–175

In terms of commercial interest 3 products are the most developed:

- Poly 3 hydroxy -co-4 hydroxy butyrate, (PHB) plus other PHA's – Metabolix.
- Poly 3 hydroxy butyrate-co-valerate (PHBV) - Tianan Biologic, (China).
- Poly 3 hydroxy butyrate-co-hydroxy hexanoate (PHBH) - Meredian.

Simple PHA's such as PHB and PHBV have melting points of around 110°C.

A typical HDT at 0.45 MPa of 143°C is higher than that for injection molded PLA products. However, as the crystalline melting point decreases with higher chain length copolymers so will the HDT.

**Water/moisture vapor transmission rate (WVTR/MVTR).**

Limited advances have been made which offer promise to ultimately overcome the limitations of high water and carbon dioxide transmission rates of PLA. Work by SIG Corporation on silicon dioxide barrier treatment for PLA films are indications of the advances being made in the film area as is the use of Nano particles in a PVOH binder. The latter approach provides good oxygen barrier at low RH but mediocre improvement at higher humidity with very little effect on WVTR. Silicon dioxide is extremely difficult to work with and is very expensive. Application of this technology to

**Table 5. Comparative Moisture Vapor Transmission Rates (MVTR).** All values are g m<sup>-1</sup> day<sup>-1</sup> for a for 50 µm film at 23C and 90% relative humidity. Table modified from<sup>41</sup>

Polymer	MVTR
Metabolix PHA	20-150
Crystalline PLA	3400
Polycaprolactone	3600
Cellulose Acetate	58400
Cellulose Propionate	34000
BOPP	3-5
LDPE	0.4-0.5
OPET	10-15
Ecoflex (BASF)	3400-3600
Nylon 6	15

injection stretch blow molded (ISBM) bottles has not been demonstrated. To date the only real solutions which can only be applied to films to reduce WVTR is metallization or laminated films<sup>40</sup>.

<sup>40</sup>. [www.polyestertime.it/files/pla\\_film\\_24042011\\_nangeroni.pdf](http://www.polyestertime.it/files/pla_film_24042011_nangeroni.pdf)

No information for the vapor transmission properties of PBS is available but it is likely they will be as poor as PLA.

According to Metabolix, the short chain length PHA's (due to their high crystallinity) have much lower WVTR than other Biopolymers. See Table 5.<sup>41</sup>

<sup>41</sup>Jim Lunt & Associates LLC. Nova-Pack 2008 Conference.

No information is available for the carbon dioxide transmission properties of PHA's.

### **Shelf Life**

As previously discussed, at normal temperature and humidity shelf life for single-use products should not be an issue. However, for multiple-use products such as cell phone casings or automotive parts, hydrolytic degradation in uncontrolled environments will be a potential issue.

Work has been carried out by Rhein Chemie<sup>42</sup> to stabilize PLA products against hydrolytic degradation during use in uncontrolled humidly and temperature environments such as electronic and automotive components. An additive – polycarbodiimide is being supplied under the trade name BioAdimide™.

Currently, there are two BioAdimide™ grades available. The BioAdimide™ 100 grade is claimed to improve the hydrolytic stability up to seven times that of an unstabilized grade, thereby helping to increase the service life of the polymer. In addition to providing hydrolytic stability, BioAdimide™ 500 XT is said to act as a chain extender that can increase the melt viscosity of an extruded PLA 20 – 30 percent compared to an unstabilized grade, allowing for consistent and easier processing. It is probable that this additive could also be used with PBS and PHA's.

<sup>42</sup>[http://lanxess.cn/uploads/tx\\_lxsmatrix/120905\\_MD2\\_Cai\\_en\\_presented\\_4-3.pdf](http://lanxess.cn/uploads/tx_lxsmatrix/120905_MD2_Cai_en_presented_4-3.pdf)

### **Melt Strength**

Melt strength or extensional viscosity is important for the successful production of blown/cast films and foams. Aliphatic polyesters have poor melt strength compared with PET and the polyolefins. There are several approaches discussed in the literature.<sup>43, 44, 45</sup>

<sup>43</sup>. <http://www.ptonline.com/products/additives-modifier-boosts-pla-melt-strength>

<sup>44</sup>. [http://www.plasticstrends.net/index2.php?option=com\\_content&do\\_pdf=1&id=218](http://www.plasticstrends.net/index2.php?option=com_content&do_pdf=1&id=218)

<sup>45</sup>. [http://www.polyvel.com/content/products/pla\\_melt\\_streng.asp](http://www.polyvel.com/content/products/pla_melt_streng.asp)

The preferred approach to improve extensional melt strength of linear polyesters is the use of branching agents. For PLA two approaches have been studied commercially- use of peroxides and multi functional epoxidised coupling agents. Peroxides to date have not been found suitable due to the creation of gels in the final product. The use of a

multifunctional epoxidised acrylic resin, which was originally manufactured by Johnson Polymers in the USA but is now supplied by BASF – **JONCRYL® GRADE 4368** has been shown to be effective in reacting with the hydroxyl and acid ends of the PLA.<sup>46</sup>

<sup>46</sup><http://www.ptonline.com/articles/materials-additives-blends-take-pla-upscale>

Similar products are also available from **Arkema** and **Clariant**. According to NatureWorks LLC., (US Patent 7,566,753), the use of this coupling agent, which has approximately 7 epoxy groups/ molecule, can have significant effect on the extensional viscosity of PLA – Table 6.

**Table 6. Improving the Extensional Viscosity of PLA**

Acrylic co-polymer (wt %)	MFR <sup>4</sup>	Die Swell	RV	PDI <sup>5</sup>
0	8.76	1.03	3.34	1.98
0.17	2.53	-	3.93	2.55
0.2	4.22	1.52	4.05	2.66
0.25	1.43	2.08	4.2	3.24

- Pellets are dried at 100<sup>0</sup> C under vacuum overnight and swept with nitrogen at 100 cc/min. Dried samples are removed from the oven, capped and run immediately.
- Melt flows are measured on a Tinius Olsen Extrusion Plastometer at 210<sup>0</sup> C with a weight of 2.16 Kg. and die diameter of 0.0825 inches. Sample pellets are loaded into the barrel of the apparatus and held there for five minutes prior to applying the load. An average of at least three measurements is collected during the melt flow runs.
- Approximately 1-inch lengths of molten polymer strand are cut off at the die and cooled. The diameter of the strands is measured and divided by the known diameter of the die to give die swell.
- Reported results are an average of at least 5 measurements relative to polystyrene standards.

PBS will probably have the same melt strength issues as PLA but no information has as yet been presented. PHA's have not been use commercially for blown films, other than in blends with small amount of PHA, so it is not known if melt strength will be an issue.

### **Tear Strength**

Linear polyester films have very poor tear strength compared to polyolefins. PLA, PBS and PHA's alone are not suitable for flexible blown films due to either being too rigid or too flexible. The typical solution is to produce blends of PLA or PHA with Ecoflex or PBS.

PLA is blended with Ecoflex by BASF to produce Ecovio™ which produces a compostable blown film by blending PLA and Ecoflex FB X 7011. The ratio of Ecoflex to PLA is 55:45 so as to maintain the Ecoflex as the continuous phase. The PLA provides renewable resource content and increased stiffness.

**Table 7. Typical Properties of 50 µm Ecovio™ film.** \*\* Two melting points are for PLA and Ecoflex.

Tensile Modulus (MPa)		Tensile Stress (MPa)		Tensile Elongation (%)		OTR (cm <sup>3</sup> /m <sup>2</sup> /24 hr)	MVTR (g/m <sup>2</sup> /24 hr)	Melting Temperature °C (**)		Haze (%)
MD	TD	MD	TD	MD	TD			PLA	Ecoflex	
750	520	35	27	320	250	600	92	140-155	110-120	58

Typical properties for Ecovio™ are given in Table 7.

Compared with PLA alone, the blend with Ecoflex results in a film with improved elongation but still high WVTR. Overall, Ecovio is suitable for films used in disposable bags and liners although it is expected that tear propagation properties will still be poor compared with polyethylene.

In 2008, Metabolix introduced a developmental flexible film grade -Mirel A5004. Mirel A5004 is said to be a partially biobased film grade designed specifically for agricultural mulch films that biodegrade in soil at ambient temperatures. A5004 is said to process easily on conventional cast and blown film equipment. A5004 is said to be a durable and versatile material with excellent melt strength and good drawdown stability for blown film processing. In addition it has excellent tensile strength and punctures toughness, good tear resistance, contact clarity, and is heat sealable. Property data is shown in Table 8.<sup>47</sup>

**Table 8. Typical Properties of Mirel A5004.** Table modified from<sup>47</sup>.

S.G. ASTM D792	Elong. at Break ASTM D882 (%)		Secant Mod. ASTM D882 (GPa)		Elmendorf Tear St. ASTM 1922 (g/µm)		Tens. St. at Break - ASTM D882 (MPa)		Coeff. Friction ASTM D1894	Dart Drop ASTM D1709 (g/µm)	Melting Point (°C)
	MD	TD	MD	TD	MD	TD	MD	TD			
1.30	400	500	0.3	0.4	1.57	3.15	30	25	0.250	7.87	170

<sup>47</sup><http://www.matweb.com/search/datasheettext.aspx?matguid=ed4f9848cf204d2291bfd427a7e01540>

All reported data is based on a 1.5 mil thick blown film (2.5 blow-up ratio) produced using a 2.5 inch extruder fitted with a 2.0 inch spiral mandrel blown film die and a dual-lip air ring.

Thermal and mechanical properties were measured after 2 weeks conditioning at room temperature. This product has recently been discontinued and replaced with similar products.

### Impact Strength

Impact strength of PLA and short chain length PHA's are inferior to competitive products such as PET and PVC.

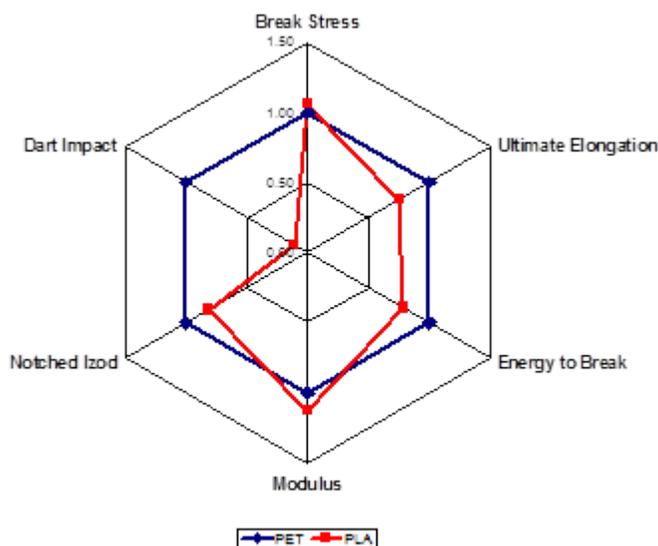
PLA is a rigid polymer and can produce brittle parts as illustrated by its poor notched Izod and falling dart impact properties. Very early work focused on using epoxidised

natural rubber in blends with natural rubber and compatibilizers to improve the impact performance of PLA. However, these blends were difficult to produce and were completely opaque. PLA was also blended with Ecoflex and PBS to improve the impact resistance but improvements were minor and clarity was again lost. Subsequently it was found that acrylic impact modifiers gave significant improvements in impact behavior. Initial products were opaque but subsequent products were transparent.<sup>48</sup>

<sup>48</sup>Great Lakes Regional ACS Meeting, Green Chemistry Symposium, May 31, 2006, Laura M. Babcock.

The acrylic impact modifiers used are the “core shell” acrylics. By slight changes in composition the refractive index of the acrylic matrix can match that of PLA. The rubber phase is small enough to allow light to pass through.

Today these modifiers are, of course, petroleum based but are highly effective at very low loadings. Figure 7 shows the initial impact performance of PLA versus its major target- PET.



**Figure 7. Impact Performance of PLA versus PET.** Figure modified from<sup>48</sup>.

Table 9 shows some of the original impact modifiers studied. More recently Rohm & Haas, Arkema, DuPont and Clariant have all announced impact modifiers for PLA based primarily on acrylic impact modifiers.

**Table 9. Impact Modifiers Studied for PLA.** Table modified from<sup>48</sup>.

Additive	Loading	Dart Impact (ft. lb)	Energy to Break (in-lb)	HDT <sup>o</sup> C (0.45MPa)	Tensile	
					Elongation (%)	Modulus (kpsi)
Blandex 338	5	13.7*	37.6	56	198	128
Clearstrength 320	5	10.6	17.4	56	97	119
Paraloid BTA 753	5	10.6	24	56	153	119
Ecoflex F	15	2.6	7.1	-	220	115
PLA	0	0.2	4.9	56**	17	131

Dart Impact based on ASTM 1709-98 on 6x6" sheets 15 mil thickness.

Tensile based on ASTM D882 on 4" dogbone samples cut from 15 mil thickness sheet, 2"/min elongation rate.

\*Test equipment maximum.

\*\* Heat distortion temperature (HDT) of amorphous PLA.

Typical acrylic impact additives, being recommended today are those supplied by DuPont, under the trade name Biomax Strong™, Rohm and Haas Paraloid BPM-500™ and Arkema Biostrength 200™.

Recently, Metabolix has advocated the use of a PHA to improve the impact and heat distortion performance of PLA.<sup>49</sup>

<sup>49</sup> [http://www.metabolix.com/sites/default/files/ANTEC-PLA\\_PVC.pdf](http://www.metabolix.com/sites/default/files/ANTEC-PLA_PVC.pdf)

However, loading of around 20% of the PHA is used which raises concerns about the economics of this approach based on announced pricing for Metabolix PHA's.

### Other issues with aliphatic polyesters

Issues not mentioned above which are specific to the particular material include:

#### Lactide reformation

Unstabilized PLA will reform the cyclic dimer known as lactide when heated. The amount of lactide reformation will depend on time and temperature. Lactide creates processing issues due to its volatility and tendency to sublime. In addition lactide in the presence of moisture readily forms lactic acid which is very corrosive even to stainless steel. To prevent lactide reformation a stabilizer is added during the manufacturing process. The specific stabilizer used by NatureWorks LLC is still proprietary, but is effective in preventing lactide reformation up to 260°C during typical melt processing. If PLA is to be used in blends with plastics that require processing temperatures above 260°C then a different stabilizer will be required.

#### Food approval for PBS

PBS is not approved for contact with aqueous foods and this will limit its acceptance in the bioplastics marketplace. It is not clear why food approval has been delayed.

### **Thermal degradation and post crystallization for PHA**

Key concerns with the short chain length PHA's such as PHB and PHBV revolve around thermal stability and crystallization. Processing above 180°C for these products can result in the rapid production of crotonic acid. Crotonic acid is a known irritant to skin and eyes and has a distinct odor. Unlike PLA, there is no known stabilizer to prevent the formation of this thermal degradation by product. Also in certain processes, the common nucleating agent and process conditions leads to incomplete crystallization of the final part. In such cases the crystallization process will continue over time. The crystals produced are much larger than the initial spherulites and often result in embrittlement of finished parts. Meredian claims to have overcome this issue with an improved nucleating agent over Boron Nitride which is the traditional nucleant for PHBV. However, no data is yet available to confirm this.

### **New technologies being developed, or still required, to overcome end use performance and processing limitations for aliphatic polyesters.**

While it is clear that significant progress has been made in mitigating many of the property issues with PLA there is still a need for further improvements. Nearly all the technologies being applied commercially today use either conventional petroleum based non-compostable additives or do not provide the process economics needed. The amounts of these additives that can be used are also limited if compostability is still a requirement. Some biobased compostable additives based on lactic acid and a diol such as LAPOL™ have been evaluated<sup>50</sup> with somewhat limited success due to performance and price.

<sup>50</sup>. <http://www.lapol.net/faqs.html>

For paper coating and foams, further improvements in melt strength will require more reactive branching agents such as epoxidised natural oils. Epoxidised soybean oil was used in the past during the polymerization process but abandoned due to gels. It is possible this could still work in the post polymerization process if effective catalysts for the reaction could be found.

For foams, higher temperature crystalline foams are needed with lower density. It may be that some form of post curing such as UV curing or cross linking could be of value here. For bottles and films, improved barrier coatings or multilayer layer structures are still needed. Finally, to really improve the heat performance of amorphous PLA and retain clarity requires the development of new copolymers.

Although copolymers of PLA are known and have been studied extensively in academia, none have ever been made at a development scale. The cost and time to completely investigate this approach is likely to be high, at least in the millions of dollars with no guarantee of success.

Two copolymer systems have been studied in the laboratory by Natureworks LLC. The first is to use a monomer referred to as morpholine dione. This monomer can be produced from the reaction of an amino acid such as alanine and lactic acid. Laboratory

studies have shown this to increase the glass transition temperature (T<sub>g</sub>), but color and the amount of the co monomer required were key issues at the time. More recently Isosorbide, derived from Sorbitol, has been of interest. This renewable resource monomer has been shown to raise the T<sub>g</sub> of PET and polycarbonate. In 2007 at the ACS conference in Boston the work to incorporate Isosorbide into PLA was presented.<sup>51</sup>

<sup>51</sup>Synthesis and Characterization of Isosorbide Carbonate: Lactide Copolymers.

Ola Betiku, Madeline Jenni, Karl Ludescher, Eric Meierdierks, James Lunt, and Joseph Schroeder\*

Neither of the above copolymer approaches to raising the HDT of PLA has been pursued commercially.

Other potentially compostable members of this class of “New Polymers” are the polyketals being produced by Segetis, PPC which is produced by Novomer and the thermoplastic starches being produced by Plantic.

## **A.2 Polyketals, PPC, TPS**

### **Polyketals**

The Polyketals being developed by Segetis are not yet truly commercial. Present applications are limited to polymeric plasticizers for PVC, solvents and detergent /soap ingredients. Segetis has a pilot plant with nameplate capacity of 80 tonnes/yr and also can toll produce over 1500 tonnes/yr of levulinic ketals-based solvents and plasticizer products.

### **Polypropylene carbonate (PPC)**

PPC is produced by Novomer from petrochemically derived propylene oxide combined with carbon dioxide or carbon monoxide. Polypropylene carbonate is an amorphous aliphatic polycarbonate with a glass transition of 40 °C. Very little other information is known about its overall properties. Its low glass transition and amorphous nature significantly restricts its utility to limited applications such as ablative binders and coatings.

### **Thermoplastic starch (TPS)**

The most well known truly thermoplastic starch products are represented by the Plantic product range,<sup>52</sup> now being marketed in the USA under the DuPont Biomax® family of products.

<sup>52</sup><http://www.plantic.com.au/>

Plantic starch products are produced by compounding a modified starch with polyvinyl alcohol or polyvinyl acetate and a plasticizer such as sorbitol, glycerol or citrate esters, for example. Stearic acid is added as a mold release/lubricant and a small amount of a surfactant such as stearyl sodium lactylate is also included. The products are water soluble and have found limited application for packaging such as Cadbury’s chocolates and potentially for foam “peanut packaging”. Typical properties of the Plantic thermoplastic starch family are given in Table 10.

**Table 10. Typical properties of Plantic Starch Products.**

Product	Density (g/cm <sup>3</sup> )	MFR (g/10 min)	Tens. Stren. (MPa)	Elongation (%)	Tens. Modulus (MPa)	Izod Impact St. (J/M)	HDT (°C)	MVTR at 38C and 50% RH (g/m <sup>3</sup> /24 hr)	OTR
2100	1.43	0.43	20	110	840	66	44	35-40	0.13
2301	1.41	0.4-1.8	7.5	210	120	78	33	-	-
2501	1.49	-	22	8	1200	37	46	-	-
2700	1.35	4.7	7.5	2	630	31	45	-	-
2702	1.38	0.3-17	11	2	760	26	45	-	-

As can be seen, the heat performance of all products is extremely low. Impact resistance can be varied over quite a range as can melt flow rate (MFR), elongation and tensile properties. The products have high MVTR as expected but good barrier to oxygen (OTR), presumably due to the poly vinyl alcohol (PVOH) content in the formulation.

Major issues are the sensitivity to moisture and the relatively low processing temperature. Low compression screws (2.2-2.8) with a 20:1 L/D typical of those used for flexible or rigid PVC are most suited to avoid shear degradation of the material.

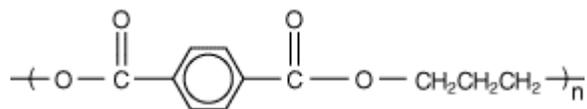
Compared with the compounded starch products from Novamont and others these TPS products are not likely to find widespread utility.

### A.3 Non-compostable new polymers

#### PTT, polyethylene furanoate (PEF), biobased polyamides

##### PTT

PTT is produced from propane-1,3 diol and terephthalic acid and although of increasing commercial interest it is not strictly “New.” PTT was first patented in 1941, but it was not until the 1990s, when Shell Chemicals developed the petrochemical route to producing high-quality 1,3-propanediol (PDO), the starting raw material for PTT, that commercial production of PTT commenced. Shell Chemicals introduced PTT under the trade name of Corterra™. PTT has the chemical structure shown below:



Corterra™ was targeted at three fiber market segments - Apparel, home furnishing and automotive fabrics. PTT was priced to be in competition with PET and nylon 6,6. Its specific gravity is 1.35 and its melting point is 228<sup>o</sup>C.

Specific key properties of Corterra PTT fabrics were claimed to be:

- Soft.
- Resistant to stretching.
- Quick drying.

- Wrinkle resistant.
- Able to retain heat-set pleats.
- Easily washed.

However, these performance advantages against PET were not sufficient for PTT to command any appreciable market share. Also, the lower melting point (compared with melting points of around 253<sup>0</sup>C- 254<sup>0</sup>C for nylon and PET) caused concern in iron ability and color fastness of apparel fabrics.

In 2000, DuPont entered the market with Sorona™ PTT in which the propane 1,3 diol was produced by fermentation. The properties are identical to the 100% petrochemical product but now the product contains 28% renewable carbon. DuPont has around 63,500 tonnes/yr Bio-PDO capacity in Loudon, Tennessee. This is equivalent to approximately 172,000 tonnes/yr of PTT. The major application appears to still be in carpets through Mohawk although the PDO is also being used by Lubrizol for biobased thermoplastic urethane products and marketed for use as a coolant in solar panels. PTT will probably not become a significant player in the bio space, particularly with developments in bio PET and bio nylon 6 and 6,6 that are underway.

#### **PEF**

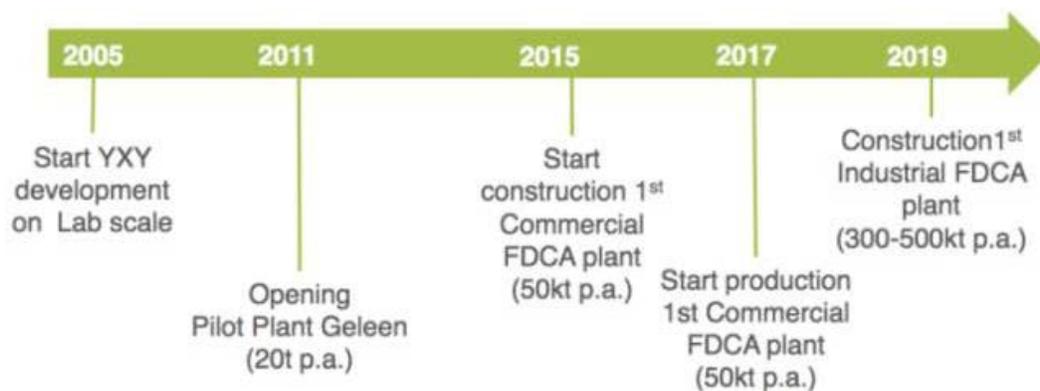
Polyethylene furanoate (PEF) is being developed by Avantium. This polymer is not yet commercial so its potential impact on bioplastics development is uncertain. PEF is produced by condensation of 2,5 furan dicarboxylic acid with ethylene glycol. Avantium is planning to combine its YXY™ molecule based on 2, 5 furandicarboxylic (FDCA) with plant-based monoethylene glycol (MEG) to produce a 100% biobased polyester-PEF.

Avantium's patented technology is said to convert biomass into Furan dicarboxylic acid (FDCA) but today glucose is the starting point. Avantium announced the start up of a 40 tonne/yr. PEF pilot plant in 2011 at the Chemelot site (Geleen, Netherlands) and plans to start commercial production of FDCA and PEF in 2016 through a 50,000 tonnes/yr. plant.

Avantium claims that PEF will compete against PET due to its higher Tg, and superior vapor barrier properties. They have formed strategic partnerships with Coca Cola, Danone and ALPLA to develop PEF bottles for personal care/home applications such as cosmetics and detergents, and for food applications such as sauces, dressings, baby foods and edible oils. ALPLA and Avantium will also work on developing PEF bottles for beer and other alcoholic beverages. On June 05, 2014 Avantium announced additional funding of €36million (\$47 million) in investments from Swire Pacific, The Coca-Cola Company, Danone and ALPLA.<sup>53</sup>

<sup>53</sup>. <http://avantium.com/news/Avantium-Raises--36M-Investment-from-Swire-The-Coca-Cola-Company-Danone-and-ALPLA>

They also provided a commercialization timeline as shown in Figure 8.



**Figure 8. Avantium Commercialization Timeline.** Figure modified from<sup>53</sup>.

### Biobased Polyamides

Nylon 11, based on castor oil, has been known and marketed by Arkema since the 1940's when it was introduced for swimwear and sun awnings. Due to high cost the marketing focus changed to higher-value markets such as hydraulic oil lines where it provides unique and differentiated performance. In the 1940's there was no interest or perceived value in its renewable resource origin.

More recently, due to increasing interest in biobased materials, other biobased Polyamides have also been introduced by several companies:

- DSM (EcoPaXX®) a 4/10 polyamide that is sourced 70% from castor oil.
- Evonik produces VESTAMID® Terra DS. This polyamide 10,10 is produced entirely from monomers obtained from castor oil.
- BASF's Ultramid Balance®, a polyamide 6-10, comprises around 60% sebacic acid which is a castor oil derivative.
- DuPont's Zytel® polyamides 6,10 and 10,10.
- Solvay and Mitsubishi Chemicals are also working together on biobased polyamides.

Since this area is exploding with new products whose success in the marketplace is too early to judge, we will focus on nylon 11 technology as representative of renewable resource based Polyamides based on castor oil.

The process to make nylon 11 from castor oil is quite involved and includes several reaction steps. Briefly, it is as follows:

Castor oil is converted to methyl ricinoleate by treatment with methyl alcohol. Methyl ricinoleate is pyrolysed at high temperature yielding heptaldehyde, methyl undecylenate and a small amount of fatty acids. Methyl undecylenate is hydrolyzed to produce undecylenic acid. When undecylenic acid is treated with hydrogen bromide in a non-polar solvent in the presence of peroxide, reverse Markownikoff addition occurs

and the main product is x-bromoundecanoic acid. This is then treated with ammonia to give x-aminoundecanoic acid, which is a crystalline solid. Aminoundecanoic acid is the starting material for nylon-11.

Nylon 11 is produced by condensation polymerization of the aminoundecanoic acid at 200-220°C to strip out water. The residual castor cake, which comprises 45-50% of the castor bean, is mainly used as a fertilizer. It is unsuitable as an animal feed because of the presence of a toxic protein called ricin and toxic allergen often referred to as CBA (castor bean allergen). However, it is noteworthy that none of the toxic components is carried into the oil.

The world castor seed production is over 900 thousand tonnes/yr India is a major producer with over 60 % share, followed by China and Brazil with about 20% and 10 % respectively. Some other countries that produce small amounts of castor beans are the West Indies and some regions of Africa.

The castor oil is transported for long distances – sometimes tens of thousands of kilometers - from the place of production to the place of consumption or conversion. From an overall sustainability perspective, the many steps required to convert castor oil to nylon 11, the low yield of castor oil and the shipping distances, all raise questions around the real sustainability of this product.

In terms of performance, nylon 11 has generally good resistance to chemicals and common solvents. The presence of the long hydrocarbon unit leads to reduced moisture absorption compared to nylon 6 and nylon 6,6 but more susceptibility to attack by hydrocarbon solvents.

Pricing for nylon 11 is around \$9-13/kg and is likely to remain around this pricing for the foreseeable future. Nylon 11 capacity is around 6,000 tonnes/yr. With its high pricing and sustainability questions, growth for nylon 11 and other biobased polyamides will be limited.

## **B. Conventional polymers developed either partially or completely from renewable sources.**

Products considered in this class of bioplastics include: Regenerated cellulose, cellulose acetate, starch blends, PET, PE, PP, PVC, polyurethanes, epoxies and unsaturated polyesters.

### **B.1 Cellulosics**

Besides the aliphatic polyesters discussed in Section A.1 the other compostable bioplastics of growing importance are the cellulose acetates. Like PLA cellulosics are transparent. Transparency is a key valued attribute in many markets such as packaging for food and consumer goods. PLA, from NatureWorks LLC, still occupies a unique position as the only easily melt processable, 100% renewable resource derived compostable product, suitable for making clear transparent thermoformed containers and films.

Recently, however, we have observed the resurgence of regenerated cellulose from Innovia films under the trade name NatureFlex™. Clarifoil also produces cellulose acetate/diacetate, referred to as ACETATE™ which is a viable candidate for compostable clear films. The Innovia product is said to be 95% renewable but is not a thermoplastic. The Clarifoil product is diacetylated to make it melt processible and appears to be plasticized. In both cases, the films are produced by the polymer manufacturers themselves by solvent casting. Also cellulose acetate is used in the Biograde™ compounded products provided by FKUR.

### **Innovia Natureflex™ Products**

Originally, regenerated cellulose was marketed as Cellophane. Cellophane film was invented in 1908 by Jacques E Brandenberger, a Swiss textile engineer who in 1900 first thought of the idea for a clear, protective, packaging layer. The cellophane process, however, was considered very environmentally unfriendly involving digesting cellulose in strong alkali, followed by adding carbon bisulfide to form sodium xanthate. This solution known as viscose was then extruded through a narrow dye into a sulfuric acid bath which regenerated the cellulose as a clear film. The film was then bathed in glycerin to make it flexible and then coated with a waxy layer to make it moisture proof. This process was modified by Eastman Kodak and the Celluloid Corporation by converting the cellulose directly to cellulose acetate using acetic anhydride. After washing with water, the cellulose acetate was dissolved in acetone to be cast as a film. Upon extruding to form the film the acetone evaporates leaving a clear film.

Recently, Innovia films reintroduced cellophane under the trade name Natureflex®. According to their information on the life cycle of this product, they still take cellulose and use alkali to produce the viscose syrup and then cast and regenerate by using an acid bath.<sup>54</sup> However, they have significantly improved the process to alleviate environmental concerns and also use only “managed” tree plantations.

<sup>54</sup>[Innovia-life cycle](#)

Natureflex™ products are supplied as cast film by Innovia. Processing information is therefore limited as are the number of potential applications to date. Un-coated cellulose films are highly permeable to water vapor whilst still providing an excellent barrier to micro-bacteria, flavors and aromas. They are naturally glossy, anti-static, provide excellent dead-fold characteristics and are receptive to printing inks. All cellulose film is heat-resistant.

Many grades of film are coated, in order to refine and control these natural attributes for specific applications and for moisture barrier. By adding specially formulated biodegradable coatings, Innovia Films claims it is able to produce films with varying levels of barrier to meet the demands of different foodstuffs.

There are several grades of NatureFlex in the marketplace, ranging from uncoated cellulose films to coated products and laminated films with other materials such as PLA, Materbi and potentially other materials. In 2006 the launch of two new grades of Innovia films were introduced:

- NVS (semi-permeable flow-wrap film for chilled food applications).
- NM (metalized) film aimed primarily at twist wrapping applications).

In 2007, NVL and NVLW (clear and white films for label applications) were also launched. In 2008, NatureFlex™ NK (a high barrier film), NVR (a heat sealable film with enhanced print and conversion receptivity) and a range of NatureFlex™ colored films were launched. Finally, in 2014, Innovia Films launched the first home compostable film designed for lidding applications, NatureFlex™ 55HK1. The new hermetic sealing film has been adopted in Italy for lidding on compostable food service trays used by schools in the Naples municipality. This new film comprises NatureFlex™ together with a proprietary sealant layer, which further increases the technical capabilities of the cellulose-based packaging film. The advantages of NatureFlex™ 55HK1 include an excellent barrier to moisture and a good aroma barrier. This is in addition to enhanced seal ability and seal integrity to a wide range of bio trays. Derived from renewable resources, NatureFlex™ 55HK1<sup>55</sup> is certified to OK Compost's Home Composting standards and to EN13432 by Vinçotte for Industrial Composting.

<sup>55</sup><http://www.innoviafilms.com/NatureFlex/News/Media-Centre.aspx?id=90>

Since this material is not a thermoplastic it is only available as a variety of cast films from suppliers such as Innovia films. During the manufacture of the film the supplier can add pigments or fillers dyes and softeners/plasticizers. Post extrusion, coatings for improved slip, adhesion, heat-seals and barrier can all be applied. Films are supplied in 20, 23, 30 and 45 micron thicknesses. Typical applications include vertical form, fill and seal (VFFS) packaging, flow wrap, twist wrap and overwrap.

### **Product Functional Performance Limits:**

#### **Hydrolytic stability**

Hydrolytic stability during manufacture is not an issue since the films are solvent cast. It would be expected that for uncoated film stored in tropical conditions, degradation would begin to occur since the films are backyard compostable which typically operate at much lower temperatures than municipal composts. NatureFlex products typically mineralize completely within 45 days in high humidity conditions such as used in the ASTM D 6400 standard. Uncoated films will need to be protected from moisture ingress.

#### **Drying**

No special drying or handling of the film on wrapping lines appears to be required.

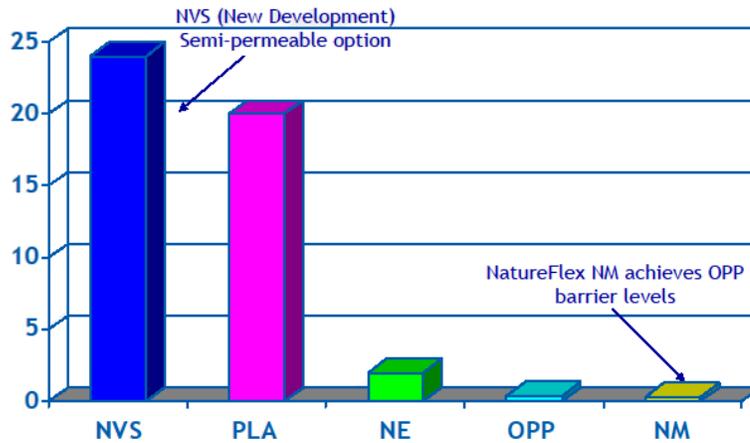
#### **Mechanical properties**

NatureFlex films are stiffer and more oriented than some other biopolymers with similar mechanical properties to Orientated PLA, which make them suitable for use on standard flow-wrap and form-fill-seal equipment. They are also static-free for easy handling. Some typical values are provided for 3 specific grades are shown in Table 11.

**Table 11. Typical Values of NatureFlex® Films.** Table modified from<sup>56</sup>.  
<sup>56</sup>[www.innoviafilms.com](http://www.innoviafilms.com)

Property	Test Method	Test Conditions	Units	NatureFlex Grade		
				NVS	NE	NP
				NVS	NE	NP
<b>MVTR</b>	ASTM-E96	38C 90%RH	g/100 in <sup>2</sup> .24hrs	360	30	N/A
<b>Oxygen Transmission</b>	ASTM F-1927	23C 0%RH	cc/m <sup>2</sup> .24hrs	3	3	3
<b>Optical Gloss</b>	ASTM D 2457	45 <sup>0</sup>		110	90	100
<b>Haze</b>	ASTM D 1003	2.5 <sup>0</sup>	%	4	6	3
<b>COF</b>	ASTM D 1894	Static dynamic		0.25 0.25	- 0.3	0.5 0.3
<b>Tens.St.</b>	ASTM D 882	23c/50% RH	MN/m <sup>2</sup> md td	125 70	125 70	125 70
<b>Elong.@ Break</b>	ASTM D 882	23c/50% RH	% md td	22 70	22 70	22 70
<b>Modulus</b>	ASTM D 882	23c/50% RH	MN/m <sup>2</sup> md td	>3000 >1500	>3000 >1500	>3000 >1500
<b>Sealing Range</b>	Innovia Test	0.5 secs. 69kN/m <sup>2</sup>	<sup>0</sup> C	90-200	80-200	No seal
<b>Seal Strength</b>	Innovia Test	135 <sup>0</sup> C/0.5secs 9Kn/m <sup>2</sup>	g(f)/25mm	>300	>400	No seal
<b>Temp Flexibility Range</b>	-	-	<sup>0</sup> C	0-290	0-290	0-290

Major differences in the grades shown are in the water vapor transmission (WVTR) and the ability to be heat sealed. These differences are probably due to the different outer layers in the laminated grades versus the Base NP grade. The basic grade has very high WVTR which is higher than PLA. More information on WVTR is given in Figure 9. The NM grade is a metalized film grade.



**Figure 9. WVTR of NatureFlex products v PLA.**

### **Heat Performance**

Coated films are readily processed on packaging lines with a very wide heat sealing range from 90°C to 200°C. The products are thermally stable under all normal processing conditions.

### **Tear Resistance**

No information is available on this property. It is to be expected that, similar to most biopolymers, tear propagation resistance will be much lower than polyolefins.

### **Impact Resistance**

For films this is not a relevant property. Puncture resistance is generally a more relevant value for flexible films but, since these products are rigid films, this again is not relevant for the uses of regenerated cellulose today.

### **Other Mechanical, Thermal or Chemical Deficiencies, UV and Oxidative Stability**

No issues are known since these films are produced by the manufacturer who controls the additives used.

### **Processing Limitations**

Originally nearly all clear packaging lines were developed to run cellophane films. These newer films are said to run extremely well on the older lines and the newer lines developed for OPP, PET and OPS films. Since the only markets occupied by Natureflex™ today are in films there are no critical issues that need to be overcome other than the need to heat seal which has been overcome today by the use of heat seal layers based on other polymers. The films are amorphous. Some limited applications in coated paper are appearing and this may be an area where laminating and adhesion to the paper may need some development.

### **Technologies being applied to overcome the various issues outlined and their efficacy to date.**

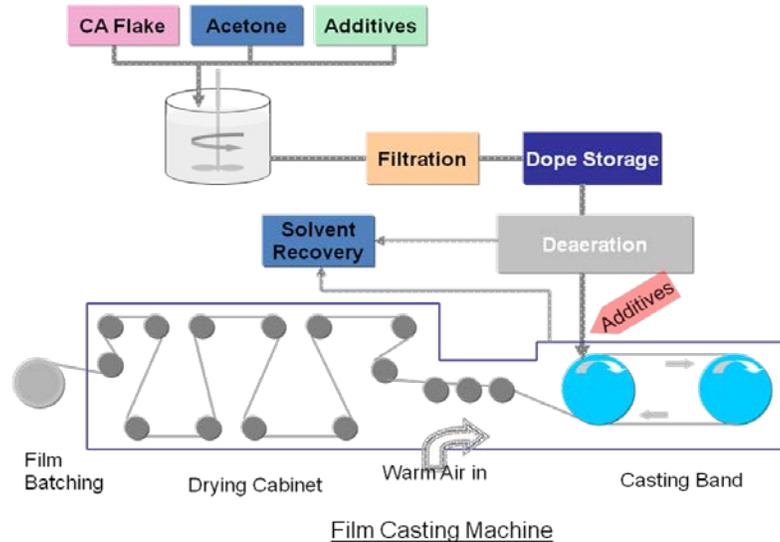
Major recent developments are in the area of heat seal ability using other biopolymers such as PLA or Mater-Bi as the heat seal layer. In addition, moisture vapor transmission has been significantly reduced by over a factor of 3 in the New NatureFlex NK coated product (WVTR = 10g/m<sup>2</sup>.24 hrs at 38°C. 90%rh.) compared with earlier products, while still maintaining transparency. These improvements have been achieved by the manufacture of trilayer films using other bioplastics as the outer layer. The bioplastic outer layer for the NK series has not been divulged. However, a laminated film consisting of 30 microns of NatureFlex, coated on two sides with a heat-sealable Mater-Bi® film is being produced by Biobag Intl. Norway.<sup>57</sup> Other laminated films with PLA are also being marketed.

<sup>57</sup>: <http://www.ptonline.com/products/converting-and-printing-bio-films>

### **Clarifoil ACETATE™**

Unlike NatureFlex™ products the Clarifoil ACETATE™ cellulose diacetate products are thermoplastics and so can be melt processed. Although cellulose diacetate alone is very difficult to be melt processed the use of plasticizers enable the material to flow under heat and pressure. Melt processable blends of this material with other materials are now being supplied under the Biograde™ product line, manufactured by FKUR.

Cellulose acetate/diacetates are produced by treating cellulose from wood pulp or cotton linters with acetic acid. The resulting cellulose acetate "flake" is mixed with a small proportion of plasticizer and traces of anti-block compound and is cast onto a continuous band to produce a non-oriented film with exceptional optical properties. A schematic of the Clarifoil process is shown below in Figure 10.



**Figure 10. Schematic of the Clarifoil Cellulose Acetate Process**

Clarifoil cellulose diacetate film is available in a number of standard formulations or grades:

- P20 is the standard, food contact formulation used in most films from 14 $\mu$  up to 95 $\mu$  thickness.
- P27 is also suitable for food contact use and is used for thicker films from 115 $\mu$  - 500 $\mu$ .
- M28 is a special grade for matt pressure sensitive tapes.
- F07 is a clear, 36 $\mu$  flame retardant cellulose acetate film.

Different plasticizers are used in Clarifoil films, depending on the end use. These include glycerol triacetate (triacetin), which is a direct food additive and can be naturally derived, as well as glycerol, citrate esters and others.

Typical film applications include:

- Print lamination in high gloss, matt, satiné and semitone.
- Invisible mending tape with easy tear characteristics.
- Window cartons, especially for food packaging.
- Label stock for tamper-evident and security labels.

- Optical film for polarized sunglasses, display screens.
- Antifogging film for sports goggles, visors and safety glasses.

**Product Functional Performance Limits**

In films, many of the attributes and limits on performance are similar to NatureFlex. Since the films are solvent cast the same technologies can be applied to both products. The key differentiating factor is that the plasticized and compounded acetate derivatives are thermoplastics and so can be melt processed. Only the differences incurred due to the melt processability will be covered in this section.

Table 12 illustrates some typical injection molded properties of Hard (non plasticized) and Soft (plasticized) cellulose acetate grades.

**Table 12. Injection Molded Properties of Cellulose Acetate.**

Properties	Units	Values	
		Unplasticized	Plasticized*
Specific Gravity		1.23	1.32
Flexural Mod.	(MPa)	2740	758
Tensile Strength	(MPa)	125	39.5
Tensile Elongation	(%)	2.2	70
Rockwell Hardness		112	38
Notched Izod Impact	(J/m)	51.0	195
HDT	(°C)	86.0	50.0

\*Plasticizer triacetyl citrate at 20% by weight.

**Application Issues**

Drying temperatures are low for most processors. Melt processable cellulose acetates have poor heat distortion properties and very poor flow characteristics. Maximum melt processing temperature is 230°C. To form relatively good parts the mold cavity must be heated leading to long cycle times. The products are amorphous and their performance will vary with moisture content.

**Technologies being applied to overcome the various issues outlined above and their efficacy to date.**

Very little work has been reported on improving the melt processability for injection molding. However, FKUR has developed their **Biograde®** cellulose blends for injection moulding, extrusion blow moulding & cast films. The grades provided include: Biograde® C9950, Biograde® C9555, and Biograde® C7500CL. Biograde (R) C7550CL is placed to compete against PLA.

**Processing of FKUR Biograde Products:**

- Pellets require drying at 60°C for 2-4 hrs.

- Pellets should be stored in a cool dry place and opened containers resealed immediately after use.
- Processable on standard injection moulding machines.
- No need for modification of screws dies or tools.
- Processing window from 190°C to 220°C.
- Cycle times comparable to PS.
- Short cooling times.
- No use of corrosive plasticisers.
- No degassing or leaking of plasticiser.
- Heat resistant up to 130°C.

**Application Issues:**

All finished products must be stored dry and at room temperature. It is recommended to seal the products in black polyethylene bags to protect against moisture and ultra violet light.

**B.2 Starch Blends.**

Blends of thermoplastic starch or starch powder occupy around 40% of today's bioplastics. Until recently three players dominated this field: Italy's Novamont, Germany-based Biotec, and USA-based Cereplast.

From a technology and sales perspective Novamont is the leader in this field (with Biotec having similar technology) Cereplast products are pure blends and in the opinion of Jim Lunt & Associates, do not have the performance of Novamont's products. Cereplast has recently filed for bankruptcy. Biotec and Novamont have been in litigation over patent rights until in 2013 when they reach an agreement to end all pending patent litigations. The contents of this agreement are still confidential. Novamont is clearly the leader and its products will be used as the benchmark for the performance of the starch blends.

Novamont was founded in 1990 in order to develop and market products manufactured by Fertec, a Montedison subsidiary whose mission was to fuse Montecatini's chemical capabilities with those of the agro-industrial Ferruzzi group. After incorporating Fertec, Novamont continued to strive to find new ways of utilizing green raw materials-resources which could be renewed from year to year. The aim was to transform these into bioplastics, biofuels and renewable chemical intermediates for low environmental impact applications, but with all of the properties of traditional products. Novamont's chief products Mater-Bi<sup>®</sup> and Origo- Bi<sup>®</sup> are biodegradable and naturally compostable. Containing renewable resources from agricultural origin, they show reduced emissions of greenhouse gases, and reduced consumption of energy and non-renewable resources. Novamont's products and technologies are protected by more than 50 patent families covering the most industrialized countries. The patent portfolio was expanded through the acquisition of the bioplastics IP of Warner-Lambert in 1997 and the Eastar Bio patents of Eastman in 2004.

The products are used in a variety of sectors: agriculture, mass market retailing, tableware, waste management, hygiene and personal care, motor industry, packaging, etc. These are all primarily film applications. Novamont supplies a variety of grades for other applications such as injection molded cutlery and plates, thermoformed and foamed parts. Manufacturing capacity today is said to be 120,000 tonnes.

The starting point for Novamont’s products is non genetically modified corn starch. The starch is first converted to a thermoplastic starch in a similar process used by Plantic. This destructure starch is then “complexed” with variable quantities of PLA or biodegradable petroleum based polymers to create a variety of molecular superstructures with a wide range of properties that can be put to many different uses.

In the broad Mater-Bi® family, the most recent ‘second generation’ grades arose out of research into raw materials obtained from vegetable oils. This new product range presents synergies with the already consolidated technology of starch processing.

In addition to its Mater-Bi® product line Novamont has the capacity to produce 0.07 million tonnes/year of Origo Bi® which is a combination of Novamont’s vegetable oil technology and Eastman’s Eastar-Bio PBAT technology which they acquired in 2004. In 2012 Novamont completed the acquisition of a business unit of Tecnogen, the biotechnology research business owned by Sigma Financial Tau SpA. The acquisition is part of Novamont’s strategy to build its biotechnology business called Mater Biotech in a joint venture with Genomatica, starting with the production of bio-based 1,4 butane diol (1,4 BDO) based on Genomatica technology. The 1,4 BDO will be used to produce a biobased equivalent of PBAT.

Typical properties of Mater-Bi are shown in Table 13. Also to allow comparison properties comparative properties of the competitive Biotec product and Cereplast product are provided.

**Table 13. Typical Properties of Mater-Bi versus Cereplast Product.**

Property	Units	Mater-Bi injection grade	Mater-Bi film grade	Biotec film grade	Cereplast injection grade
Density	g/cm <sup>3</sup>	1.33	1.29	1.3	1.28
Melt temp	°C	146	110	-	-
MFR	g/10min	3	3	2.5-5.5	11
Elongation	%	160	340	600-900	5.1
Tens. Modulus	MPa	1100	210	-	-
Flex. Modulus	MPa	-	-	-	3360
Break Load	MPa	19	22	20-35	49.6
HDT	°C	-	-	-	44
WVTR	Various*	-	850 gx30 micron/m x 24 hr.	120g/m <sup>2</sup> day	-
OTR	cm <sup>3</sup> /m <sup>2</sup> day	-	-	750	-

Starch-based products all have high WVTR but relatively low oxygen transmission. Their sensitivity to moisture makes them acceptable in short shelf life compostable applications only. Mater-Bi materials are certified 'biodegradable and compostable' under the EN13432 and EN14995 standards for Europe and under the ASTM D-6400 standard for the United States, and some materials have received similar compostability certifications (AS 4736 in Australia, GreenPLA system in Japan). The certifying bodies operating in the biodegradable and compostable plastics sector are CIC-Certiquality (Italy) DIN CERTCO (Germany) and VINÇOTTE (Belgium).

The heat performance of the Mater-Bi products is higher than the Cereplast product due to the incorporation of Ecoflex which has a crystalline melting point of 110-120<sup>0</sup>C. Cereplast products, which contain PLA, are typically amorphous and so do not show a melting point. The temperature performance of these products will therefore be much lower. Toughness or ductility of the Novamont products would also be expected to be superior to the PLA products due to the ductility of the Ecoflex.

The gas transmission properties are difficult to compare due to the various units, temperature and humidity used in the testing. However, it can be stated that the starch based products all have high WVTR but relatively low oxygen transmission properties in common with other compostable bioplastics.

Tear initiation for these films is generally accepted to be comparable to LDPE. However, tear propagation is very low. There are no known critical issues with UV oxidative or chemical resistance for the short shelf life, single-use markets these products presently serve. Sensitivity to moisture is an issue but again not in the market segments presently being addressed.

### **Product Functional Performance Limits:**

#### **Hydrolytic Stability**

Typical shelf life of these products before opening is 6 months. In hot humid climates the products will degrade and so must be protected from extremes of temperature and humidity.

#### **Drying**

All starch based products are hygroscopic and will pick up moisture on storage. If moisture pick up has occurred it is recommended the material be dried at 80<sup>0</sup>C for 2 hours.

### **Processing Limitations**

For all the starch products, typical processing recommendations include:

- Maximum melt temperature of 200<sup>0</sup>C
- Relatively flat temperature profile of 150-180<sup>0</sup>C

- Feed throat should be cooled
- Melt temperature 150-190°C
- General purpose screw with typically a 2.5-3.0 compression ratio and 20:1 to 25:1 L/D
- Cold or hot runners can be used for injection molding
- Mold temperatures recommended by Cereplast are 10-27°C
- Mold temperatures recommended by Novamont are 18-40°C.

In all cases the machine must be purged, typically with HDPE, both before and immediately after processing the starch based products. High temperatures above 220°C should be avoided and materials should not be left in the machine for prolonged periods of time unless the temperatures are reduced below 160°C.

For blown film, typical machines used for LDPE are recommended. Processing throughputs are lower than conventional resins either due to the low softening point requiring longer cooling cycles, or slower crystallization of the synthetic polymer in the formulation.

Also, typical of the bioplastics, melt strength for the starch based formulations is low, leading to difficulties in achieving good non friable low density foams and a thin coherent layer for paper coating. However, some of these difficulties are being overcome.

### **Application Issues**

The starch based products are not targeted at durable or multiple use applications. Their sensitivity to moisture makes them acceptable in short shelf life compostable applications only. Some grades are being trialed for blow molded products but as yet these applications are limited. Injection molding applications for the non Ecoflex containing products are limited by their heat resistance. Films appear to be the preferred application for the Novamont products.

### **Technologies being applied to overcome the various issues outlined above and their efficacy to date.**

Since the starch based products are all compounded materials, the manufactures already use blends and compatibilizer technologies to optimize cost/performance in their targeted markets. Particular formulations are patented or maintained as trade secrets.

### **New technologies being developed, or still required, to overcome end use performance and processing issues by application.**

The starch based formulations rely upon compounding of the right ingredients to achieve performance. Further improvements are likely as blends with cellulose acetate products are investigated for their potential. Of particular interest will be the use of PHA's as to their ability to reduce WVTR, improve heat resistance and potential to

improve tear propagation resistance. However, the high pricing of the PHA's may limit how much they will be used unless higher margin applications can be developed or lower priced PHA's become available.

### **B.3 PET, PE, PP, PVC.**

The properties and processing of these materials will be equivalent to their 100% petroleum based counterparts as will the technologies used to modify their performance.

The key issue with all of these materials is technology viability, economics and supply. For bio PET, only the ethylene glycol component can presently be produced from renewable resources although significant development efforts are underway to produce bio terephthalic acid (TPA). These efforts and the companies involved will be discussed in section C.

For bio polyolefins and PVC, as already discussed, the emergence of large quantities of cheap shale gas appears to be affecting initiatives in this area. For bio PVC, concerns around dioxins and the vinyl chloride monomer will still exist even if produced from renewable resources.

### **B.4 Polyurethanes, Epoxies and Unsaturated Polyesters.**

Thermosets have been largely ignored in discussions around bioplastics even though the global market is expected to experience double digit growth from 2012 to 2016 reaching 105 million tonnes by 2016.

Key thermoset materials include unsaturated polyesters (UP) and phenol-formaldehyde (PF) which together account for approximately 30% of the total global market. Other products include polyurethanes and epoxy/polyepoxide resins. The thermoset polyurethanes (PU) market alone is expected to reach 31 million tonnes by 2016. The replacement of the polyol component of polyurethanes by renewable alternatives has already begun, as well as the epoxy component and diol components of epoxies and unsaturated polyesters. For the phenol formaldehyde resins attempts are underway to replace some of the phenol by lignin or replace the PF resin completely by soy based adhesives but so far have had limited success.

#### **Polyurethanes**

Polyurethanes were introduced commercially in 1954. They are extremely versatile plastics, available in a variety of forms ranging from flexible or rigid foams to elastomers, coatings, adhesives and sealants. PURs are prepared by reacting two components: a polyol and an isocyanate. The polyol component can be produced from renewable resources such as soybean oil, castor oil, sunflower oil, and rapeseed oil.

Depending on the chosen building blocks and their origin, the renewable content of commercially available bio-based polyols is said to vary between 30-100%. Consequently, the achievable renewable content of PURs based on different

formulations also can vary substantially among different products and applications, with a typical range of range of 22% to 70%.<sup>58</sup>

<sup>58</sup><http://www.icis.com/resources/news/2012/09/21/9597480/acc-cpi-pu-players-going-green/>

The most common bio polyols today are based on soy bean oil or glycerol. Several companies including Cargill and the Dow Chemical Company are already involved in the manufacturing of these compounds. Early issues associated with the problems of consistency and odor, impact on physical properties and processing limitations, which hampered attempts to make bio-based polyols for production of flexible foams, seem to be largely overcome.

### **Epoxy resins**

Some noteworthy developments have occurred in biobased epoxy resins.

EcoPoxy (Providence, R.I.) introduced a soy based range of epoxy adhesives in 2009.<sup>59</sup>

<sup>59</sup> <http://www.ecopoxysystems.com/>

EcoPoxy makes a line of epoxies, hardeners, topcoats and adhesives with a soy-based feedstock. EcoPoxy's annual capacity is said to be around 9000 tonnes. No information as to actual sales or technology is available although it is believed the products are based on glycerol derived epichlorohydrin.<sup>60</sup>

<sup>60</sup> <http://forum.woodenboat.com/archive/index.php/t-143341.html>

Also in the thermoset epoxy resins area a company called Entropy Resins<sup>61</sup> has introduced a line of epoxy resins based on pine oil derived from wood pulp components referred to as "Super-Sap". They also claim to use vegetable oil components derived from the waste stream of bio-fuel processing in their epoxy products. The Entropy epoxy resins are said to have a bio-based carbon content ranging from 17 to 25 percent.

<sup>61</sup> <https://entropyresins.com/why-use-super-sap/>

The ready availability of glycerin as a byproduct of biodiesel is driving developments in bio based epoxy resins based on epichlorohydrin. The diglycidyl ether of Bisphenol A (DGEBA) is derived from Bisphenol A and epichlorohydrin and is one of the most common building blocks for commercial epoxy resins. The global demand for epichlorohydrin was estimated to be 1.38 million tonnes in 2012 and projected to grow by 4.8% annually till 2017.<sup>62</sup>

<sup>62</sup> <http://www.marketsandmarkets.com/Market-Reports/epichlorohydrin-market-936.html>

The synthesis of epichlorohydrin or dichloropropanol from glycerol was described in the literature and patents in the 1920s-1930s by reacting glycerol with hydrochloric acid in the presence of acetic acid or other catalysts. In 2005, Solvay patented the epichlorohydrin production from glycerol via 1,3-dichloropropanol and in 2007, Solvay began operating a 91,000 tonnes plant for the production of epichlorohydrin based on their patent.

In 2012, Solvay announced its Thai affiliate Vinythai would bring online a second new production plant in Taixing, China.<sup>63</sup> The plant, with an initial capacity of 91,000 tonnes of epichlorohydrin per year, required an investment of EUR 155 million (\$203 million) and was planned to be operational in the second half of 2014. There have been no further updates as to the status of this new plant.

<sup>63</sup>[http://www.solvay.com/en/media/press\\_releases/20120611-epicerol-china.html](http://www.solvay.com/en/media/press_releases/20120611-epicerol-china.html)

In 2013, AkzoNobel and Solvay signed a three-year agreement whereby AkzoNobel would increase the use of renewable raw materials in its epoxy paints and coatings. Under the terms of the deal, AkzoNobel will progressively increase the use of Solvay's bio-based epichlorohydrin, or Epicerol®, which is already contained in many of the company's resins for its coatings products. Bio epichlorohydrin is identical to its petrochemical counterpart so the only concerns are economics and supply of glycerol.

### **Unsaturated polyesters**

The global demand for unsaturated polyesters was 3.9 million tonnes in 2012.<sup>64</sup>

<sup>64</sup><http://marketssize.blog.com/files/2014/04/Unsaturated-Polyester-Resin-Market-2013-to-2019.pdf>

Unsaturated polyesters are experiencing strong growth, mainly due to the rising demand from end-use markets associated with wind energy applications such as wind blades, nacelles, rotors, nose cones, and ventilation. Unsaturated polyester resin is one of the most commonly used resins in the industry due to a competitive advantage of low price over other resins such as polyurethane, vinyl ester, and epoxy resins.<sup>65</sup>

<sup>65</sup><http://www.12newsnow.com/story/25680935/unsaturated-polyesters-market-demand-driven-by-high-growth-in-wind-energy-applications-new-report-by-micromarket-monitor>

Unsaturated polyesters are produced by the polycondensation of unsaturated and saturated dicarboxylic acids with diols such as propylene glycol (PG). Approximately 40-45% of the globally produced PG is used as intermediate for the synthesis of unsaturated polyester resins. The global market for PG is estimated to be around 544,000 tonnes/yr.<sup>66</sup>

<sup>66</sup><http://www.digitalrefining.com/data/articles/file/2040605169.pdf>

Historically, propylene glycol has been produced by hydrolysis of propylene oxide which is obtained from the cracking process of unrefined petroleum. Recently companies such as Ashland, Cargill, ADM, Dow Chemicals and BASF and others have shown interest in producing PG from a renewable resource. In March 2011, ADM began production of PG from glycerin in its 90,000 tonnes plant in Decatur IL. In June, 2012, Oleon and BASF celebrated the opening of their 18,000tonnes PG from glycerin plant in Ertvelde, Belgium. However, Global Bio-Chem Technology in China who has been operating their 190,000 tonnes PG facility announced in March this year that they were suspending all their polyol activities.<sup>67</sup> How this will affect their bio PG activity has not been disclosed.

<sup>67</sup><http://www.hkexnews.hk/listedco/listconews/sehk/2014/0331/LTN20140331893.pdf>

These recent developments in bio propylene glycol (PG) from glycerol produced from soybeans or sorbitol from corn have accelerated the expansion of bio based unsaturated polyester resins.<sup>68</sup>

<sup>68</sup>. <http://www.compositesworld.com/articles/green-resins-growing-up>

Ashland introduced its Envirez™ product line nine years ago and applied it first in a body panel for a John Deere tractor. Since then, the product line has expanded to cover almost all manufacturing processes and end-markets, including construction, energy, automotive and solid surface. The bio-based content in the Envirez products ranges from 8 to 22 percent, depending on the application and intended manufacturing process. The company's bio-based monomers make Envirez resins more expensive than their all-petrochemical counterparts. The price of most bio-based Envirez resins is 10 percent above conventional petro-based resins. Resins made with recycled content don't carry this surcharge. This restricts the market for a bio-based UPR to customers whose preference for the green aspects of the resin outweigh the additional cost. This is particularly true of customers that manufacture composites for the construction market, where the U.S. Green Building Council's Leadership in Energy and Environmental Design (LEED) program encourages use of recycled or bio-based materials.

Reichhold (Research Triangle Park, N.C.) has also developed its own bio-derived resins.<sup>69</sup>

<sup>69</sup>. <http://www.reichhold.com/en/composites-products.aspx?cat=Brands&pid=171>

The products are trade named ENVIROLITE™. Reichhold says ENVIROLITE's bio-source is proprietary, but its bio-content ranges from 12 to 35 percent. The resins are designed for sheet molding compound (SMC), bulk molding compound (BMC), pultrusion and cast-polymer applications. It's also said to be a drop-in replacement for traditional general-purpose UPR. Reichhold also cites the LEED program as a significant driver in this market, but also points to the U.S. Department of Agriculture's BioPreferred program, which promotes increased use of bio-based products.

Renuvix<sup>70</sup> has recently introduced Esseneo™ Sucrose Polyester Resins which are said to be based on sucrose esters of vegetable oils and feature a compact molecular structure, a high number of reactive functional groups, as well as a variety of different reactive functional groups to choose from. Esseneo™ resins can be used in the formulation of paints and coatings, composites, adhesives, and lubricants. Renuvix has also developed copolymers of vinyl ether functional oleochemicals which are trade named Averde™.

<sup>70</sup>. <http://renuvix.com/>

No other public domain information is available on Renuvix.

### **C. New/existing renewable “building blocks” or monomers/oligomers for new and existing polymers.**

In 2010, with the announcement by Braskem of its green polyethylene from bio ethanol, several other biobased monomer initiatives have subsequently been announced. Rather than looking at new bioplastics which require considerable expense and time to commercialize, the bioplastics

activities have essentially refocused on the development of “drop in” replacements for the existing chemical building blocks. These monomers are chemically identical to their petrochemical counterparts and so can be used in the existing capital assets in place. However, since the starting point is no longer oil, new infrastructure may be required to actually produce these intermediates. There are many initiatives underway to produce a wide range of monomers from renewable resources – Figure 11.<sup>71</sup>

<sup>71</sup>Tecnon OrbiChem Marketing Seminar, APIC 2013, Taipei, 9 May 2013.

However, the most commercially interesting examples of these monomers include adipic acid, hexamethylene diamine (HMD), glucaric acid, succinic acid, ethylene glycol, butane diol, caprolactam, terephthalic acid and acrylic acid. In addition “new” chemicals such as furan dicarboxylic acid (FDCA), isosorbide and propane, 1, 3 diol are also worthy of mention since these monomers cannot readily be produced petrochemically.

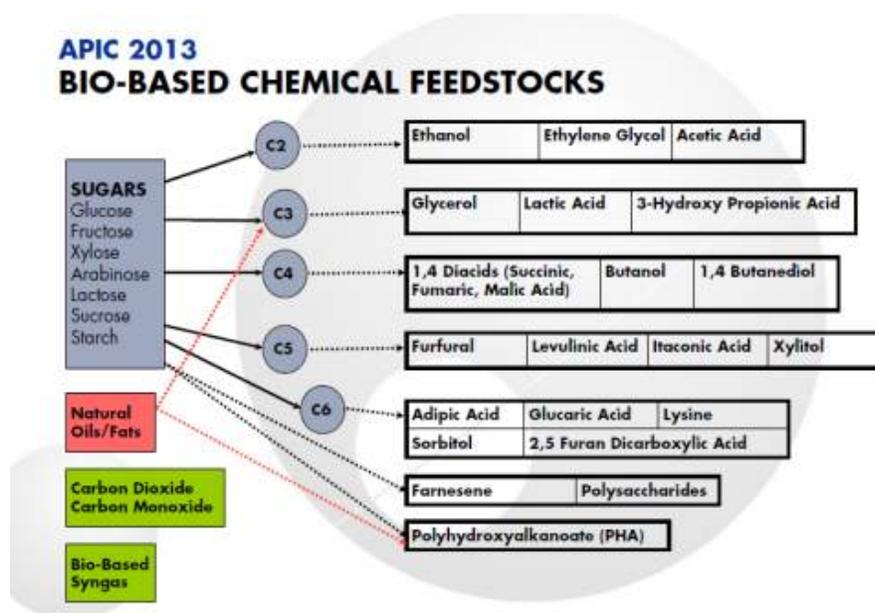


Figure 11. Bio Based Chemical Feedstocks. Figure modified from<sup>71</sup>.

## C.1 Conventional Monomers

### C.1.1 Adipic Acid

Global petrochemically derived adipic acid (ADA) demand was estimated at 2.3 million tonnes in 2012 and growing at 3–5% per year.<sup>72</sup> Nylon 6,6 accounts for about 85% of the total adipic acid demand. The other applications are polyurethanes (5%), adipic esters (4%), and others (6%). Major global producers of ADA include Invista, Ascend, Honeywell, BASF, Radici, China Shenma, and PetroChina. The average price was \$1.60/kg in 2012. High-purity fiber-grade adipic acid is used to make nylon 6,6, while lower purity adipic acid is used primarily to produce polyurethanes.

<sup>72</sup><http://www.ihs.com/products/chemical/technology/pep/bio-based-adipic-acid.aspx>

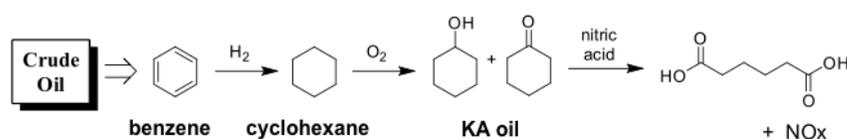
Start-up companies such as Rennovia, Verdezyne, BioAmber, Celexion, and Genomatica are developing bio-based routes to produce adipic acid. Two of these companies- Rennovia and Verdezyne are presently considered the leaders.

Rennovia (Menlo Park, CA), an early-stage start up founded by researchers at Symyx Technologies, is developing a chemo-catalytic process for production of adipic acid from renewable raw materials. The company raised \$12 million in venture backing led by 5AM Ventures (Menlo Park, CA) and Versant Ventures (Redwood City, CA). In March 2014, ADM committed to a \$25 million equity investment in Rennovia, Rennovia is targeting a commercial demonstration unit for its bio-adipic in 2014.

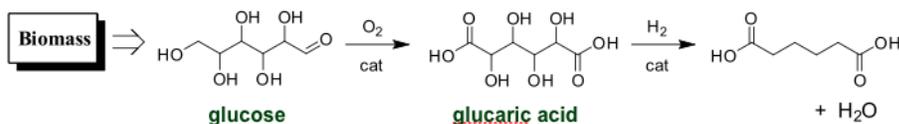
According to Rennovia, preliminary cost estimates on its adipic acid process have found that it is below the cash-cost of the conventional cyclohexane process. The company is seeking partnerships with existing producers of adipic acid.

Rennovia uses air oxidation to convert glucose to glucaric acid, followed by hydrodeoxygenation to convert glucaric acid to adipic acid- Figure 12.

**Current petrochemical process via cyclohexane:**



**Rennovia renewable adipic acid process:**



- Broad IP filed
- Preliminary cost estimates below cash-cost of cyclohexane process

**Figure 12. Petrochemical and bioprocess for Adipic Acid.**

Rennovia contends that the chemo catalytic approach to making chemicals has advantages over biotechnology. In addition to being well established, chemical catalysis offers technical advantages. According to Rennovia chemical catalysis provides more degrees of freedom in the pH, temperatures and pressures that can be used compared with fermentation. Rennovia's glucose feedstock sourcing will come from existing carbohydrate supply chains, and eventually shift toward non food-based raw materials as those supply chains mature.

In March 2014, Rennovia and Johnson Matthey Davy Technologies<sup>73</sup> announced a collaboration to develop, demonstrate, and commercialize catalytic process

technologies for the production of bio-based glucaric acid and adipic acid. Under the collaboration, Rennovia and JM Davy will work together to develop and demonstrate the processes based on Rennovia's technology for the catalytic aerobic oxidation of glucose to glucaric acid, as well as the catalytic hydrogenation of glucaric acid to adipic acid. The goal of the collaboration is to develop and jointly license a technology package enabling commercial production of these chemical products.

<sup>73</sup><http://www.biofuelsdigest.com/bdigest/2014/03/23/rennovia-and-johnson-matthey-davy-technologies-to-collaborate-for-glucaric-acid-adipic-acid-project/>

### **Verdezyne, Inc.**

Verdezyne is a privately held synthetic biology company. Verdezyne have patented an engineered yeast fermentation route to adipic acid which they estimate could have at least a 20% cost of manufacturing advantage for bio-based adipic acid depending on the feedstock selected. Presently, Verdezyne is engineering the metabolic pathway to boost organism performance. In 2011 they started up a small pilot plant capable of producing approximately 700kg of bio-based adipic acid/yr. In parallel, Verdezyne continues to make metabolic pathway improvements to utilize renewable feedstocks such as sugar.

On April 28, 2014, Verdezyne announced it had negotiated key terms for an investment of \$48million led by Malaysian multinational conglomerate, Sime Darby Berhad.<sup>74</sup>

<sup>74</sup><http://verdezyne.com/wp-content/uploads/VerdezyneSime-DarbyreleasePOTUSFINAL.pdf>

The funds will be used to accelerate Verdezyne's technology development in the U.S. and support various collaborative projects with Sime Darby's newly formed business unit, Sime Darby Renewables.

Led by Sime Darby, this \$48 million financing for Verdezyne was joined by existing investors BP Alternative Energy Ventures, DSM Venturing B.V., OVP Venture Partners, and Monitor Ventures.

### **C 1.2 Hexamethylene Diamine (HMD)**

Hexamethylene diamine is the other key monomer in the manufacture of nylon 6,6. Rennovia is a key player that, in addition to adipic acid, claims to have a biocatalytic route to convert glucose to HMD - See Figure 13.



**Figure 13. Rennovia Process for Hexamethylene Diamine.**

Hexamethylene diamine is currently produced from petroleum-derived propylene or butadiene. Rennovia said it has developed a lower cost route of directly producing HMD from sugars without going through the bio-adipic acid process.

Nylon 6,6 is used in resin and fiber applications as well as in polyurethanes. End markets include exterior/interior/under-the-hood automotive parts, coatings, tires, carpeting and consumer goods such as shoes and apparel.

With Rennovia being able to produce both bio-based adipic acid (ADA) and bio-based HMD, the company is now able to develop a 100% bio-based nylon 6,6.

The company said production costs for its bio-based HMD are projected to be 20%-25% below that of conventional petroleum-based HMD with significantly lower per-pound capital cost. Projected benefits for the bio-based chemical also include a 50% reduction greenhouse gas emissions compared to conventional petroleum-derived HMD.

Rennovia's next step is to produce bio-based HMD (and bio-based ADA) at a demonstration scale. Rennovia says it has already refined its glucaric acid-based adipic acid process after more than 18 months of pilot plant operation.

The company is targeting a commercial demonstration unit for bio-adipic acid by 2014 with a fully integrated "mini-plant" designed to allow direct scale-up to the full commercial scale of 120,000 tonnes/year. Rennovia anticipates its first commercial-scale production in 2018. Rennovia is confident that its bio-based adipic acid will be highly cost-competitive not only against petroleum-based ADA but

also other bio-based ADA routes that are currently being developed. Aside from Rennovia, other companies in the bio-based ADA development space include Verdezyne, BioAmber, DSM and Genomatica.

Conventional adipic acid production is currently via oxidation of cyclohexane. Major global producers of adipic acid, according to consulting firm IHS, include Invista, Ascend, Honeywell, BASF, Radici, China Shenma and PetroChina. Average adipic acid price last year was estimated at \$1.60/kg and according to IHS, Rennovia's and Verdezyne's processes both have a high potential to be cost competitive since both bio-routes are said to have the advantage of using \$0.30/kg of glucose feedstock compared to cyclohexane that had a market price of \$1.25/kg last year. However, significant challenges for the bio-based routes, according to IHS<sup>75</sup>, include Rennovia's ability to achieve high feedstock selectivity and catalyst productivity, and in the case of Verdezyne, high enzyme turnover rates and satisfactory kinetics for Verdezyne's enzyme fermentation route.

<sup>75</sup><http://greenchemicalsblog.com/2013/04/24/rennovia-updates-bio-nylon-feedstock-developments/>

### C 1.3 Glucaric Acid

Glucaric acid has been known for many years with applications ranging from preventing corrosion on bridges to producing polymers. The US Department of Energy recognized glucaric acid as one of the "top twelve building block chemicals" that can be subsequently converted to a number of high-value chemicals or materials. However, the markets for glucaric acid derivatives such as bio-based glucarates and lactones are said to be undeveloped as they are expensive and the supply has been limited, with most being use for research or as a health supplement ingredient.

Rivertop Renewables was founded in early 2008 in Missoula, Montana, where the corporate headquarters is located. Rivertop Renewables has announced they are working on glucaric acid for a variety of uses including adipic acid as a building block for Plastics. In the section on Rennovia discussed above, glucaric acid is actually a primary intermediate in their process to make adipic acid.

The conventional commercial route to glucaric acid involves the oxidation of cyclohexanol using nitric acid. The byproduct, nitrous oxide is said to be difficult to capture and re use leading to high waste. The Rivertop process involves the oxidation of glucose and captures the nitric acid and waste lost by other processes and efficiently recycles it back into the input stream.



Figure 14. Rivertop Renewables Process to Glucaric Acid.

Glucaric acid has the following physical properties:

Physical state and appearance: Solid (Powdered solid or crystalline powder.)

Odor: Odorless.

Molecular Weight: 300.27 g/mole

Color: White

Melting Point: >250°C (482°F)

Solubility: Insoluble in cold and hot water, almost insoluble in ethanol.

Rivertop Renewables recently announced that it has raised \$26 million in its Series B investment round from Cargill, First Green Partners and existing investors. Rivertop will leverage these funds and an existing manufacturing relationship to produce market development quantities of salts of glucaric acid for select customers. In addition, it will complete construction and begin operations at a semi-works facility at its headquarters in Missoula, where it will optimize its process for world-scale deployment. Rivertop plans to hire more than 20 employees in the next 12 months to support commercial development, effectively doubling the size of its workforce.

Rivertop's initial focus will be on commercializing opportunities in the dishwasher detergent and corrosion inhibitor markets. The company will explore additional opportunities from among several large industries including home and personal care products, oil and gas, agriculture and food. According to Rivertop this represents a potential addressable market of over 36 million tonnes/year with values between \$0.39 and \$1/kg.

#### **C 1.4 Succinic Acid**

Succinic acid has historically cost \$3-\$5/kg, depending on the prevailing oil price, which is much higher than other four-carbon platforms such as petroleum-derived maleic anhydride which sells at about \$1.50/kg. That lower price explains why maleic anhydride represented a market of 1.6 million metric tonnes in 2008, eclipsing succinic acid and consigning it to niche applications. For biobased succinic acid it is believed it can easily compete on price with conventional succinic acid and ultimately with maleic anhydride. The current breakdown for petrochemical derived succinic acid markets is shown in Figure 15.

The estimated global succinic acid market was 40,000 tonnes in 2011 of which only 3% was biobased at this time. This picture is now changing.<sup>76</sup>

<sup>76</sup>. [http://www.bioconcept.eu/wp-content/uploads/BioConSepT\\_Market-potential-for-selected-platform-chemicals\\_report1.pdf](http://www.bioconcept.eu/wp-content/uploads/BioConSepT_Market-potential-for-selected-platform-chemicals_report1.pdf)

Succinic acid currently has a market worth of \$225 million. Market research firm Frost & Sullivan believes the market will expand to over 180,000 tonnes by 2015 thanks largely to the introduction of biosuccinic acid.<sup>77</sup>

<sup>77</sup>. <http://www.rsc.org/chemistryworld/News/2010/January/21011003.asp>

Interest in succinic acid derived from renewable resources has accelerated considerably with at least 4 companies now in the advanced stages of commercialization. One of the

largest emerging applications for succinic acid is the production of 'green' 1, 4-butanediol (BDO), a chemical widely used in a range of applications including the production of engineering plastics, Lycra (spandex) fibers and solvents with estimated annual production of around 1.4 million tonnes a year. Combining BDO and biosuccinic acid also opens up the possibility of biopolymers, such as polybutylsuccinate (PBS), which is used in biodegradable packaging films and disposable cutlery. The market for PBS is currently small - around 10,000 to 15,000 tonnes a year - but could swell with a 100 per cent biobased product. Another potential market is in polyester polyols and polyurethanes, currently dominated by the use of adipic acid as a precursor. Companies are looking at replacing the six-carbon adipic acid with four-carbon biosuccinic acid, providing the costs become comparable. Present routes to adipic acid are considered environmentally unacceptable and produce a lot of carbon dioxide.

Key players in the biobased succinic acid field include:

BioAmber, Myriant, Succinity (a joint venture between BASF and Corbion/Purac), and Reverdia (a joint venture between DSM and Roquette).

### **BioAmber**

BioAmber is presently the leader in bio succinic acid commercialization and as such will be covered in detail.

The origins of BioAmber's succinic acid business go back to 1995, when they were established as Applied CarboChemicals. BioAmber itself was established in December 2008 as DNP Green Technology. In the fall of 2009, DNP Green Technology completed a \$12 million financing with a group of institutional investors led by Sofinnova Partners, a leading European venture capital firm, and including Mitsui & Co. Venture Partners, the venture arm of the Japanese trading powerhouse Mitsui & Co, and Samsung Ventures and the venture arm of the Samsung Group, one of Asia's largest industrial groups. Other investors were the Clifton Group, a Canadian based real estate group with interests in clean tech, and AquaRIMCO, a Japanese investment fund.

Since the spin off in 2008, BioAmber has established several business partnerships and has successfully commissioned an industrial scale production facility. It has also moved down the value chain through its acquisition of Sinoven Biopolymers.

In the fall of 2010, DNP Green Technology acquired 100% of the shares of its BioAmber joint venture from ARD. Concurrent with the acquisition of the joint venture, DNP Green Technology changed its name to BioAmber Inc. Diversified Natural Products contributed its intellectual property portfolio and ARD agreed to build an industrial scale production facility in France, at a cost of €21 million (approximately \$27 million).

Last September Mitsubishi signed a deal with Thai company PTT to develop biosuccinic acid-based PBS. The JV is called PTT-MCC Biochem. PTT-MCC was established to develop and produce biobased polybutylene succinate (PBS). The company is currently building its first PBS plant in Map Ta Phut, Rayong, Thailand, with a capacity of 20,000 tonnes/year. The PBS plant is expected to be operational in the first half of 2015, and will consume around 14,000 tonnes/ year of succinic acid at full capacity, just in time for

BioAmber's start-up in early 2015 of its 30,000 tonnes/ year bio-succinic acid plant in Sarnia, Ontario, Canada.<sup>78</sup>

<sup>78</sup>. <http://greenchemicalsblog.com/2014/05/19/ptt-mcc-signs-bio-succinic-acid-contract-with-bioamber/>

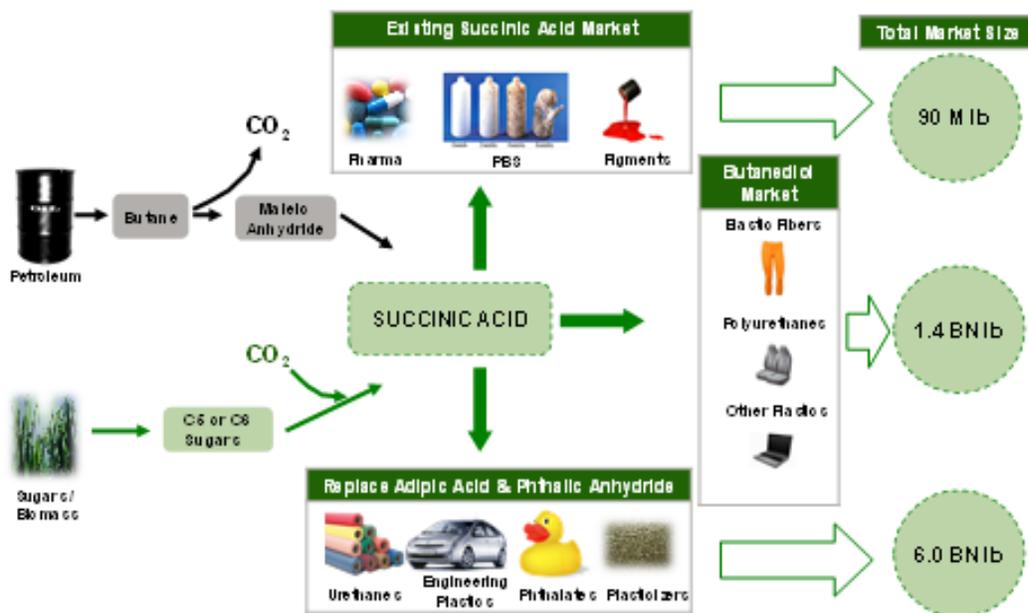


Figure 15. Markets for Succinic Acid - Courtesy Myriant

After the commissioning of both the Sarnia bio-succinic acid plant and PTT- Mitsubishi Chemicals (PTT-MCC) PBS plant in Thailand, BioAmber will exclusively supply a minimum of 80% (1 million tonnes/year) of PTT-MCC's total bio-succinic acid needs until the end of 2017. The take-or-pay volume committed by PTT-MCC over the 3-year period represents half of the total annual quantity of bio-succinic acid that PTT-MCC plans to purchase from BioAmber.

The company uses a proprietary yeast that it has exclusively licensed from Cargill. Cargill originally developed the yeast for the production of lactic acid and has been using the yeast at commercial scale for over four years. The yeast has the ability to ferment at a low pH and tolerate high concentrations of succinic acid, giving it a distinct advantage over other organisms producing succinic acid via fermentation which cannot tolerate low pH. BioAmber collaborated with Cargill in the development and scale up of the succinic acid yeast and achieved the final milestone in September 2013. BioAmber has designed its commercial plant in Sarnia to operate with the yeast technology.

BioAmber has also licensed from DuPont a catalyst technology that can convert bio-based succinic acid into bio-based 1,4-Butanediol. The technology involves the liquid phase hydrogenation of succinic acid into 1,4-Butanediol (BDO), Tetrahydrofuran (THF) and Gamma-Butyrolactone (GBL). The products are then separated and purified through distillation. DuPont originally commercialized the technology in Spain in a plant that converted maleic acid into THF.

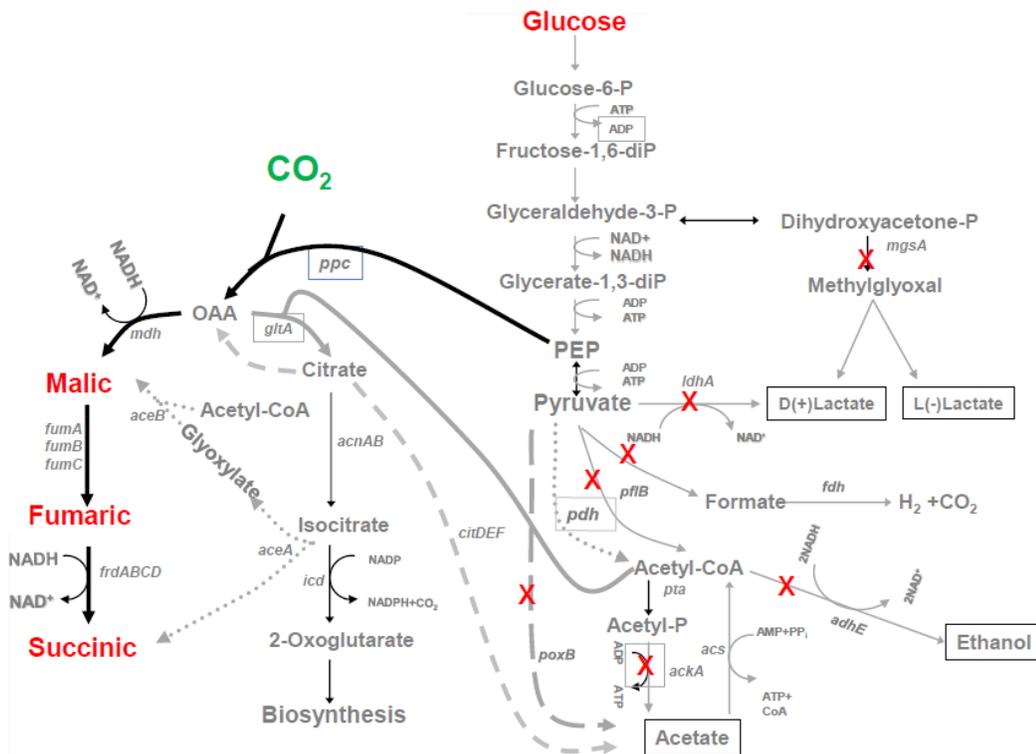
BioAmber has partnered exclusively with Evonik to further develop and optimize the catalyst compositions licensed from DuPont, so that they efficiently convert succinic acid instead of maleic acid. Evonik will be the exclusive supplier of commercial grade catalyst to BioAmber and DuPont will receive a royalty on sales. In February this year, BioAmber Inc. and Vinmar International, Ltd. (Houston, TX) signed a take-or-pay contract for the purchasing of 100% of the BDO produced in a 90,000 tonnes/yr capacity plant that BioAmber plans to build in North America and commission in 2017. Furthermore, Vinmar plans to invest in BioAmber’s first BDO plant to be located in the US.

Finally, BioAmber has also exclusively licensed the Cargill yeast for the production of bio-based adipic acid and exclusively licensed a metabolic pathway from Celexion, a Boston-based biotech company. The pathway enables the production of bio-based adipic acid, hexamethylene diamine (HMD), caprolactam, hexanediol and caprolactone, using fermentable sugars.

### Myriant

US-based Myriant, which spun out of bioethanol specialist BioEnergy International, is among the companies which see major potential for biosuccinic acid. Myriant believes total penetration of bio succinic acid in conventional applications would equate to a \$10 billion market. In 2010 Myriant obtained a \$50 million grant from the US Department of Energy to help build a commercial-scale facility in Louisiana.

In 2011, the company was making biosuccinic acid at the 20,000 liter bioreactor scale using modified *E. coli* bacteria and unrefined sugar as a feedstock. Their proposed pathway is shown in Figure 16.



**Figure 16. Myriant’s proposed pathway to succinic acid.** Pathway construction in the organism involves knocking out genes to provide for all carbon and energy to be used for succinic acid production.

Also in 2011, PTT iThailand announced they had invested \$60 million in Myriant to build a commercial facility in Lake Providence, LA which is said to be capable of producing around 14,000 tonnes of bio-succinic acid annually. The facility began operations in 2013. The second plant, in cooperation with their global alliance partner, ThyssenKrupp Uhde, is located in Leuna, Germany and has a capacity of 1,500 tonnes/ year. In February 2014, Myriant announced it had supplied commercial quantities of bio-succinic acid to Oxea, for use in the production of bio-based, phthalate-free plasticizers. On January 8 of this year, Myriant filed a request with the SEC asking for the withdrawal of its registration statement. Myriant originally announced its plans to proceed with an initial public offering (IPO) in May 2011. No further announcements have been made.

#### **Succinity (BASF and Corbion JV)**

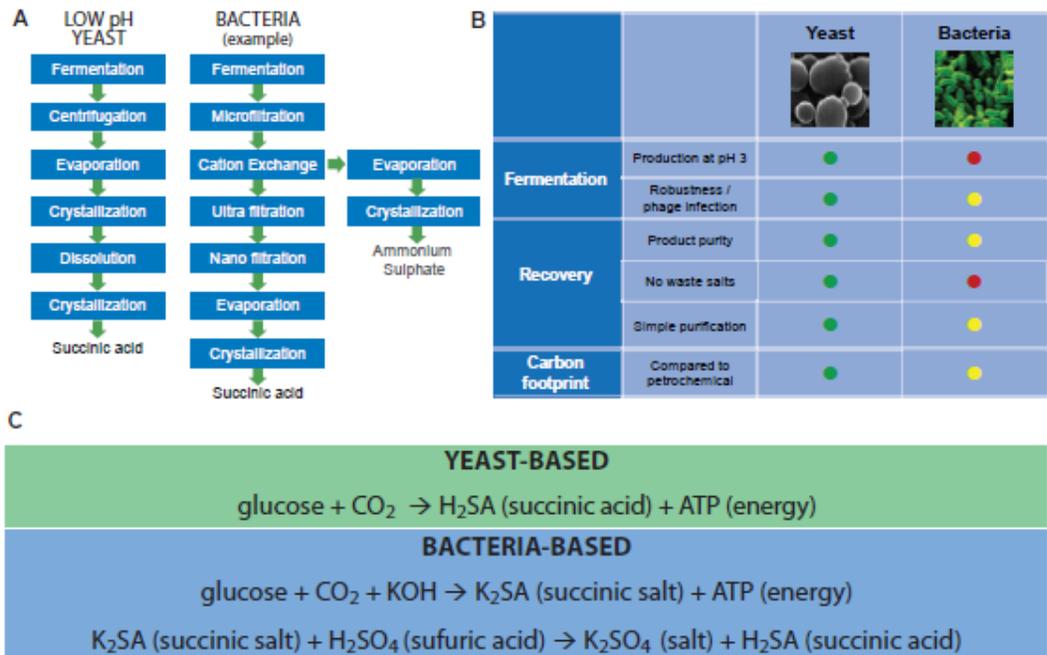
BASF and Corbion Purac have been working on the development of biobased succinic acid since 2009. Succinity GmbH, the joint venture between Corbion Purac and BASF for the production and commercialization of biobased succinic acid, just announced the successful start-up of its first commercial production facility located at the Corbion/Purac site in Montmeló, Spain. The plant has an annual capacity of 10,000 tonnes/yr and is producing commercial quantities of biobased succinic acid for the global market.<sup>79</sup>

<sup>79</sup>. <http://www.basf.com/group/pressrelease/P-14-0303-CI>

Succinity uses the microorganism *basfia succiniciproducens* which is said to be a natural producer of succinic acid and can process a wide variety of C3, C5 and C6 renewable feedstocks, including biomass. Today it is believed that glucose is the feedstock. The closed-loop process produces biobased succinic acid without major waste streams.

#### **Reverdia (DSM/Roquette JV)**

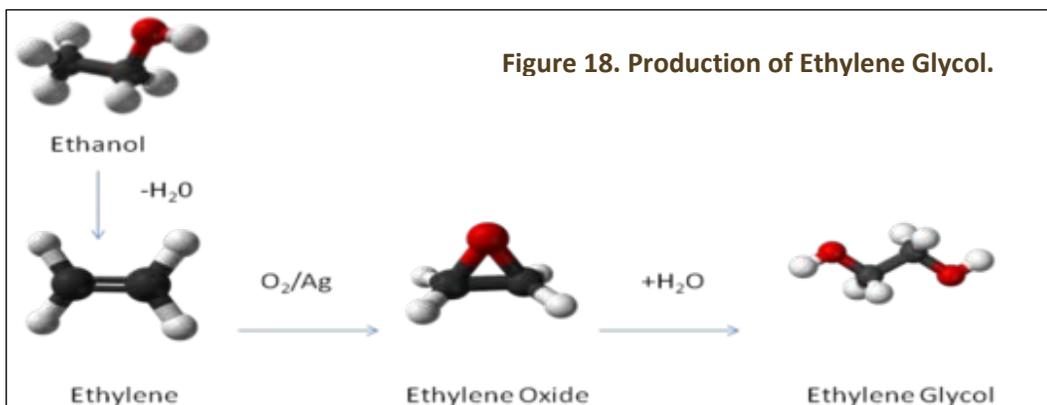
DSM is already one of the major producers of fossil-derived succinic acid. In early 2008, DSM formed a partnership with France's Roquette Frères to develop biosuccinic acid, and the two companies have been supplying kilo-scale samples from a pilot plant at Roquette's site in Lestrem, France. In December 2012 Reverdia began operations at their commercial plant in Cassano Spinola, Italy, which has a capacity of 10,000 tonnes/yr. Reverdia claims to have developed a proprietary yeast fermentation process, and are initially using glucose as a feedstock. The claimed advantage of yeast versus bacterial fermentation is shown in Figure 17. Reverdia believes it can achieve full economies of scale at around 50,000 tonnes/year.



**Figure 17. Claimed advantages of yeast versus bacterial fermentation.** Comparison of the yeast versus bacterial production processes for succinic acid: low-pH yeast technology requires fewer steps than the bacterial process (A). Additionally, it reveals a beneficial carbon footprint (B), and delivers acid instead of salts (C). With Reverdia’s proprietary low-PH (<3) yeast-based fermentation process, the succinic acid is present as H<sub>2</sub>SA. In the case of bacterial-based fermentation, since base is added to control the pH, the succinic is present as a salt (K<sub>2</sub>SA). This salt has to be transferred into acid – for example, through the addition of H<sub>2</sub>SO<sub>4</sub>. Alternatively electrodialysis can be used to convert the succinic salt to succinic acid, but this requires significant amounts of energy.

### C 1.5 Ethylene Glycol

Ethylene Glycol (MEG) is typically produced from ethylene which is produced by naphtha cracking. It can be made from ethylene made from ethanol. Ethylene can be produced from ethanol as discussed under the section on Braskem’s initiatives. Bio ethylene glycol is produced by the catalytic oxidation of ethylene as shown in Figure 18.



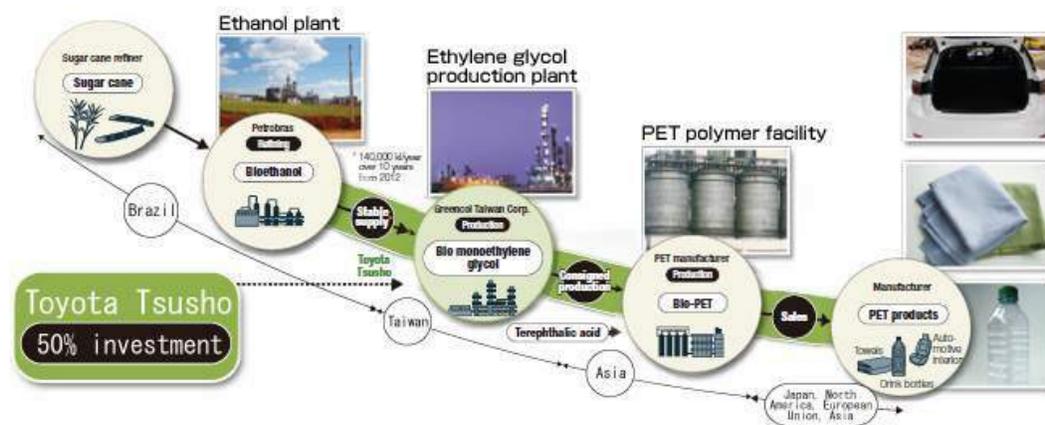
This process was actually used commercially until the early 1960's when it became more cost effective to produce ethylene and the downstream glycols from oil. Bio ethylene glycol is chemically identical to the conventional oil derived product. However, economics today still favor the petrochemical route. Today's pricing for bio MEG has a price premium of \$1.50-2.50/kg over conventional MEG.<sup>80</sup>

<sup>80</sup> [http://www.orbichem.com/userfiles/Promotions/bm\\_13\\_09.pdf](http://www.orbichem.com/userfiles/Promotions/bm_13_09.pdf)

In 2011, about 620,000 tonnes biobased PET were produced from bio MEG and this was projected to grow to a production capacity of nearly 5 million tonnes in 2020.<sup>81</sup>

<sup>81</sup> [http://www.bio-based.eu/market\\_study/media/13-03-6PRMSBiopolymerslongnova.pdf](http://www.bio-based.eu/market_study/media/13-03-6PRMSBiopolymerslongnova.pdf)

Prior to 2011, India Glycols (IGL) was the only commercial producer of polymer grade bio MEG in the world. IGL has been manufacturing bio-MEG derived from bio-ethanol since 1989, and has met the stringent international specifications as required by the polyester fiber, yarn, film and PET resin industries. Its declared capacity is 150,000 tonnes/yr. In 2012 Toyota Tsusho's joint venture company, Greencol Taiwan, with chemical firm China Man-made Fiber Corp. (CMFC) started operating its 100,000 tonne/yr bio-MEG plant in Kaohsiung, Taiwan. Bio ethanol is being secured by Toyota Tsusho from Petrobras in Brazil and converted to MEG by Greencol Taiwan. The resulting bio-MEG is shipped by Toyota Tsusho to PET toll manufacturers in Asia, and the off-take bio-PET is then marketed by the company to end users in Japan, Europe and the



**Figure 19. Toyota Tsusho's Bio PET Supply Chain.**

US. A schematic of Toyota Tsusho's supply chain is shown in Figure 19 below:

In Oct. 2012, JBF Industries Ltd. of Mumbai, India announced that under its JV with Coca Cola, it would build the world's largest facility to produce bio ethylene glycol in Araraquara, Sao Paulo, Brazil. Construction on the new facility was expected to be complete in October 2014. At full capacity, it was estimated the facility would produce 500,000 tonnes of bio ethylene glycol per year. In the 2014 Q1 report from JPF it was announced that the bio MEG facility has been put on hold.<sup>82</sup> There has been no mention of the facility in subsequent quarterly reports.

<sup>82</sup>. [http://www.jbfindia.com/new\\_pdf/JBF%20-%20Q1FY14%20-%20Earnings%20Presentation.pdf](http://www.jbfindia.com/new_pdf/JBF%20-%20Q1FY14%20-%20Earnings%20Presentation.pdf)

Other companies claiming to have dedicated a part of their PET capacities to the production of bio PET are Teijin and Indorama Ventures (both located in Asia), with capacities of 90,000 tonnes and 270,000 tonnes/yr respectively. However, it is believed they are probably purchasing the bio MEG from Toyota Tsusho. Far Eastern New Century in Taiwan (FENC) received the “Global Sustainable Procurement Supplier of the Year” award in 2013 from Coca-Cola. Aiming to be the world’s largest Bio-PET manufacturing site, FENC is planning to build a new plant in Yangzhou, China, with a design capacity of 800,000 tonnes.

In March 2012, M&G started 3 kg/hr bio-EG pilot plant in Rivalta, Italy, using lignocellulosic ethanol. The company has now completed a 44,000 tonnes/year bioethanol plant in Crescentino, Italy, which was officially commission in October 2013. The bio-ethanol plant is expected to be a future supply source for it’s bio-EG. In addition, M&G is also looking to build a cellulosic ethanol plant either in Brazil or Mexico as well as a chemicals production unit integrated to the plant that will initially produce bio-based glycols and at a later stage, bio-para-xylene (the feedstock for producing bio-PTA).

This biorefinery is expected to have 350,000 tonnes/year cellulosic ethanol, and 100,000-150,000 tonnes/year bio-glycols capacity. According to M&G, the biorefinery could be up and running in 2015. 100% of the bio-EG output will be consumed by M&G on a long term basis for use at M&G PET plants in the Americas.

In 2013, M&G Chemicals announced its decision to construct a second-generation bio-refinery in the region of Fuyang, Anhui Province of China for the conversion of one million tonnes of biomass into bio-ethanol and bio-glycols. The bio-refinery will employ PROESA™ technology licensed from Beta Renewables, a joint venture between Biochemtex (a company belonging to the Mossi Ghisolfi Group), US private equity fund TPG and Danish enzyme producer Novozymes.

Much of the initiative around the production of bio MEG and its use to produce bio PET is due to Coca Cola. Coca-Cola introduced its PlantBottle Technology in 2009 as the first recyclable PET plastic bottle made partially from plants. Since then more than 18 billion PlantBottle packages have reached the market in 28 countries, saving more than 400,000 barrels of oil. The company plans to convert all of its PET plastic bottles – which accounts for approximately 60 percent of its packaging globally – to PlantBottle packaging by 2020. In just a few short years, The Coca-Cola Company has expanded from producing PlantBottle™ plastic in a single location to now having facilities in most of their major markets, with further expansion to come.<sup>83</sup>

<sup>83</sup>. <http://www.coca-colacompany.com/plantbottle-technology/driving-innovation-coca-cola-and-ford-take-plantbottle-technology-beyond-packaging>

In 2012, The Coca Cola Company, Ford Motor Company, H.J. Heinz Company, NIKE Inc. and Procter & Gamble announced the formation of the Plant PET Technology Collaborative (PTC), a strategic working group focused on accelerating the development

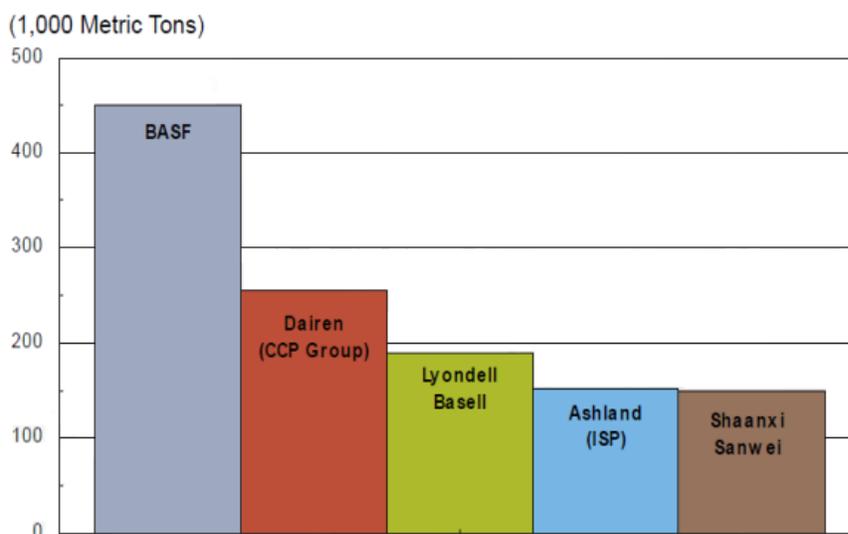
and use of 100% plant based PET materials and fibre in their products. When such brand corporations join forces and build alliances, their impact on the supply chain becomes inevitably visible. This influence has now encompassed the development of bio derived terephthalic acid (TPA), butane diol, caprolactam, terephthalic acid and acrylic acid. In addition “new” chemicals such as Furan dicarboxylic acid (FDCA), isosorbide and propane, 1, 3 diol are also worthy of discussion since these monomers cannot readily be produced petrochemically.

### C 1.6 Butane Diol (BDO)

World demand for 1,4 butane diol (BDO), according to Tecnon Orbichem, was 1.9 mill. tonnes in 2012 and projected to reach 4.3 million tonnes by 2015.<sup>84</sup> The major uses for BDO are in the manufacture of THF, gamma butyrolactone, PBT and polyurethanes. THF as well as being a useful solvent is also the precursor for the production of Spandex or Lycra.

<sup>84</sup>. <http://www.orbichem.com/apic2014.aspx>.

Major end uses for BDO in 2012 include THF (42%), PBT (26%), gamma butyrolactone (14%) and polyurethanes (16%). The major producers and their market share are shown in Figure 20.



**Figure 20. Major Global Producers of 1,4 Butane Diol in 2014.**

Figure modified from<sup>84</sup>.

Currently, the majority of BDO installed capacity is based on the conventional acetylene based process although several other processes exist.

LyondelBasell manufactures 1,4-butanediol in a multi-step process without the use of acetylene. Propylene oxide is first converted to allyl alcohol which is then hydroformulated to 4-hydroxybutyraldehyde. Hydrogenation of the aldehyde yields 1, 4-butanediol. BDO is also manufactured on an industrial scale from maleic anhydride in the Davy process in which BDO is first converted to the methyl maleate ester and then hydrogenated. Other known routes are from butadiene, allyl acetate and succinic acid.

### **Acetylene based process (Reppe Chemistry)**

Acetylene-based BDO production is the most common process which still accounts for about 40 percent of the global BDO capacity. Key producers still using the Reppe chemistry include BASF and Ashland (formerly ISP). The Reppe process is also particularly popular in China. In this process acetylene is reacted with formaldehyde to form butynediol (BYD) which then undergoes high-pressure hydrogenation to form BDO. The efficiency of the technology focuses on acetylene purification (via calcium carbide from coal) in conjunction with a proprietary catalyst and reactor technology, followed by BDO refining steps. The produced BDO undergoes ring closing chemistry to form THF.

Recently biobased processes to BDO have attracted interest. Three companies are key players in this field all using different approaches:

#### **(a) Fermentation of sugar directly to BDO and THF (Genomatica)**

Genomatica is clearly the leader in the manufacture of bio derived butane 1,4 diol. This material and route to production is becoming of increasing interest as the petro based industry moves from Naphtha cracking to natural gas which will create a deficiency in C3 and C4 hydrocarbons such as propane and butane and their downstream derivatives.

Genomatica was founded in 2000 by research scientists and engineers from the University of California, San Diego, with initial financing from Iceland Genomic Ventures. The company has been awarded government funding from the National Institutes of Health (NIH), the National Science Foundation (NSF), the Department of Energy (DOE) and the Department of Defense (DOD).

On August 2, 2012, Genomatica announced it had raised an additional \$41.5 million in a Series D round of preferred stock financing. The investment featured strategic partners, including new investor and partner Versalis, the largest Italian chemical company. Existing investors Alloy Ventures, Draper Fisher Jurvetson, Mohr Davidow Ventures, TPG Biotech, VantagePoint Capital Partners and Waste Management also joined the new round.<sup>85</sup>

<sup>85</sup><http://www.genomatica.com/news/press-releases/genomatica-raises-41.5-million/#sthash.mmlFiAmJ.dpuf>

Since June 2011, Genomatica has been producing BDO at its demonstration-scale facilities in Decatur, Illinois, U.S. – owned and operated by the food ingredients company, Tate & Lyle. Tate and Lyle are using their existing propane 1,3 diol plant and in 2013 they announced the completion of a production campaign which spanned five weeks and produced more than 2,000 tonnes of BDO.

Genomatica's process uses an engineered microorganism for the direct fermentation of sugars to BDO and potentially THF via cyclization in an acidic fermentation medium. The company claims it can process BDO produced from sugar to greater than 99 percent purity using a cost-effective recovery process. The new process begins with producing BDO in fermentation broths generated by microbes engineered to directly produce BDO from sugars, and uses process designs and

equipment compatible with large-scale chemical production. The E. coli bacteria are cultivated in large fermentation tanks on a diet consisting of sucrose and water. The bacteria then metabolize the sucrose into succinic acid and then into 1, 4-butanediol.

Genomatica has also established multiple high level corporate partnerships with key industry players across several bio chemical platforms:

#### **BASF**

May 2013, BASF and Genomatica jointly announced that BASF plans to produce BDO from renewable feedstocks using Genomatica's GENO BDO™ process technology. The license agreement allows BASF to build a world-scale production facility that uses Genomatica's GENO BDO process. BASF is the #1 producer of petrochemical derived BDO. In November 2013, BASF announced they had produced commercial volumes of BDO using Genomatica's process and began offering it to customers for testing and commercial use.

#### **Novamont**

January 2012, Genomatica and Novamont announced an agreement to establish a joint venture (JV) for the first industrial plant in Europe producing butanediol (BDO) directly from renewable feedstocks. Novamont will have a majority of the equity in the JV, and Genomatica a minority interest. Novamont, a leading producer of biodegradable bioplastics, will use the BDO internally to meet the increasing demand for its biopolymer products that incorporate BDO. Under the agreement, Novamont is converting a facility in Adria, Italy to use Genomatica's GENO BDO™ process and will fund up to \$50 million in plant investment. Novamont will also operate the plant, which is expected to have a production capacity of approximately 18,000 tonnes/yr. The agreement also contemplates Novamont building and operating a second BDO plant using Genomatica's process, which is expected to use biomass sugars as the renewable feedstock.

#### **Mitsubishi**

February 2012, Genomatica announced an agreement with Mitsubishi Chemical Corporation to exclusively negotiate definitive agreements for a joint commercial operation in Asia for the production of BDO using Genomatica's process technology.

#### **Lanxess**

June 2013, Lanxess and Genomatica jointly announced that Lanxess had successfully made poly butylene terephthalate (PBT) in their commercial-scale plant using 20 tonnes of BDO made with Genomatica's GENO BDO™ process. They were able to make PBT based on Genomatica's BDO in one of their commercial-scale plants, without any changes in their equipment or processes.

#### **DSM**

October 2013, DSM announced they had approved BDO made with Genomatica's GENO BDO™ process for use in their Arnitel product lines. By using bio BDO they are able to increase the bio-based content of their Arnitel products to as high as 73%.

### **Toray**

April 2013, Toray Industries, Inc., and Genomatica jointly announced that Toray had produced a bio-based PBT using BDO made with Genomatica's GENO BDO™ process. Toray was the first company to publicly announce PBT polymerization using BDO made with Genomatica's process. Toray also has the distinction of having produced the first PBT 'pellets' from Genomatica's BDO samples in February 2011. Toray plans to produce a bio-based PBT at commercial scale using BDO made with the GENO BDO process and planned to share samples of bio-based PBT with its customers during 2013 to help develop market demand.

### **Versalis**

Versalis, a partner in Genomatica's butadiene development program, announced an agreement in April 2013 to create a joint venture for bio-based butadiene. The companies will work together to develop a complete 'end-to-end' process for the on-purpose production of butadiene from non-food biomass.

### **Braskem**

Braskem joined Genomatica's butadiene development program through a joint development agreement announced in December 2013. Under the agreement, Braskem anticipates funding Genomatica's development work over several years; will allocate Braskem R&D resources; and fund the construction of pilot and demonstration-scale butadiene plants. Braskem will receive license rights to use the resulting process technology in the Americas; Genomatica will receive fees and royalties for each licensed commercial plant.

### **M&G**

Genomatica has a strategic partnership with Gruppo Mossi & Ghisolfi (M&G), its Chemtex engineering division and its Beta Renewables joint venture. M&G is one of the world's largest producers of PET and a leader in chemical engineering and renewable processes through its Chemtex engineering subsidiary. Its Beta Renewables joint venture has invested over \$200 million in the development of its PROESA® process for making cost-effective sugars for bio-products from non-food energy crops or agricultural waste. In January 2012, as part of the overall strategic relationship, Genomatica announced it had secured exclusive worldwide rights to PROESA for the production of BDO from cellulosic biomass, through any fermentation-based process. Additionally, the companies plan to produce BDO from biomass at demonstration-scale at Beta Renewable's facility in Rivalta Scrivia, Italy.

## **(b) Esterification followed by hydrogenolysis of succinic acid (Myriant/DPT)**

Myriant has already been discussed under bio based succinic acid production. Myriant partnered with Davy Process Technology in March 2011, focusing on engineering a process to produce BDO (as well as THF and GBL derivatives) using biosuccinic acid produced by Myriant as a straight substitute for maleic anhydride in Davy Process Technology's process. On June 12, 2013 –Myriant Corporation and Johnson Matthey - Davy Technologies (JM Davy) announced the successful production of bio-butanediol (BDO) and tetrahydrofuran (THF) made from Myriant's bio-succinic acid. The qualification work was conducted at JM Davy's facility at

Teesside, England using bio-succinic acid supplied by Myriant and the JM Davy BDO/THF process. By combining the efficiencies of Myriant's bio-succinic acid process and the JM Davy BDO/THF process, the bio-butanediol and bio tetrahydrofuran has an overall carbon efficiency of 87%, which is claimed to be substantially better than the carbon efficiency achieved in the direct fermentation process route to BDO practiced by Genomatica.<sup>86</sup>

<sup>86</sup><http://www.myriant.com/media/press-releases/myriant-corporation-johnson-matthey-davy-technologies-produce-bio-based-butanediol-at-competitive-cost-level.cfm>.

### (c) Hydrogenation of succinic acid (BioAmber)

BioAmber's previous work focusing on the production of bio-based succinic acid has led to the development of a process to convert biosuccinic acid to BDO. In 2010, BioAmber licensed DuPont's hydrogenation catalyst technology to make bio-BDO and bio-THF from biosuccinic acid. Since then, efforts have focused on scaling up DuPont's technology to produce 100 percent bio-based BDO, THF, and GBL.

## C 1.7 Caprolactam

Caprolactam is the monomer for nylon 6. Conventional caprolactam technology is based on the key intermediate cyclohexanone, which is usually produced by the oxidation of cyclohexane, but can also be made from phenol or toluene. Separately, hydroxylamine sulphate is manufactured by the oxidation of ammonia to nitrous oxide followed by hydrogenation in the presence of sulphuric acid. The hydroxylamine sulphate is then reacted with the cyclohexanone to produce cyclohexanone oxime. This is followed by a Beckmann rearrangement using oleum to yield caprolactam.

A disadvantage of existing technology is that large amounts of ammonium sulphate - up to 4.5 tonnes/tonne of caprolactam are produced. Significant development work is concentrating on reducing or even eliminating this byproduct. For example, DSM's HPO-plus process has substantially reduced this byproduct to 1.5 tonnes/tonne of caprolactam.

DSM has studied a bio-based route to nylon 6 but this effort did not move past the research stage due partly at least the fact that DSM has implemented a cheaper petrochemical route to nylon 6, effectively raising the hurdle (i.e. the difference in cost price of the bio-based monomer and the petrochemical-based monomer) for the bio-based route (DSM, 2003).

The most recent entrant to biobased caprolactam was Draths. Draths technology converts glucose to lysine to amino caprolactam to caprolactam. Improvements in the yield of L-lysine microbially synthesized from glucose coupled with the increased demand for this amino acid suggest that L-lysine could be an attractive starting material for production of caprolactam. Using synthetic organic methodology developed at Draths, they claimed to be achieving a 60% (mol/mol) yield of sublimed caprolactam from L-lysine.

Draths Corporation was founded in December 2005 to commercialize technology developed in the laboratory of John Frost and Karen Draths. A research facility was established in Okemos, Michigan, and the first employees were hired in April, 2007. In 2011 Draths was purchased by Amyris and the activity to produce caprolactam appears to have essentially stopped with the acquisition.

### C 1.8 Terephthalic Acid (TPA)

Several patented technologies have been proposed for the manufacture of TPA from renewable resources. However, the companies most active in this area are Gevo, Virent and Annelotech. Gevo and Virent are sponsored by Coca Cola who is driving for a 100% bio PET for their bottled products. Other players such as VTT in Finland, Micromidas, M&G, U Mass Amherst, Incisor and Vertichem have also claimed routes to para xylene, the precursor to TPA, but their activities are very embryonic. An overview of the various proposed routes to bio TPA is shown in Figure 21.

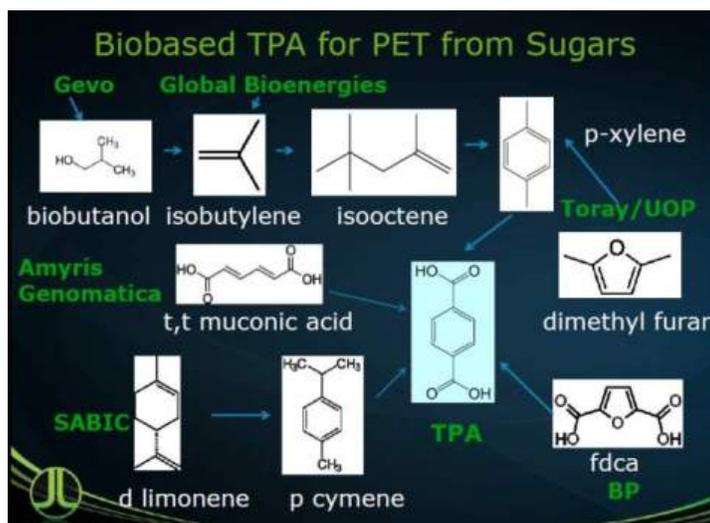
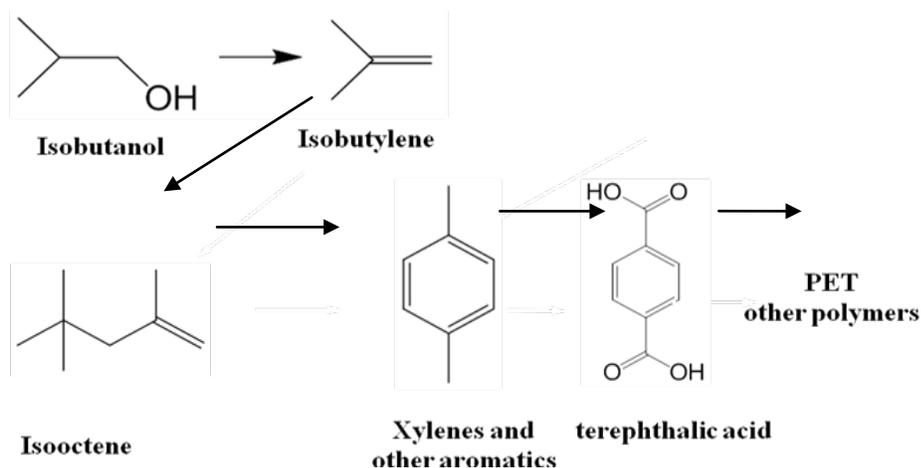


Figure 21. Proposed Routes to Bio TPA.

## Gevo TPA route

Gevo was founded by Kosla Ventures in 2007 and is actively involved in the commercialization of bio- isobutanol as an alternative fuel to bio ethanol. They are also developing a route to bio p-xylene which is the precursor molecule for TPA. Their proposed pathway is shown in Figure 22 below:

**Figure 22**  
Gevo's proposed route to Bio P-Xylene

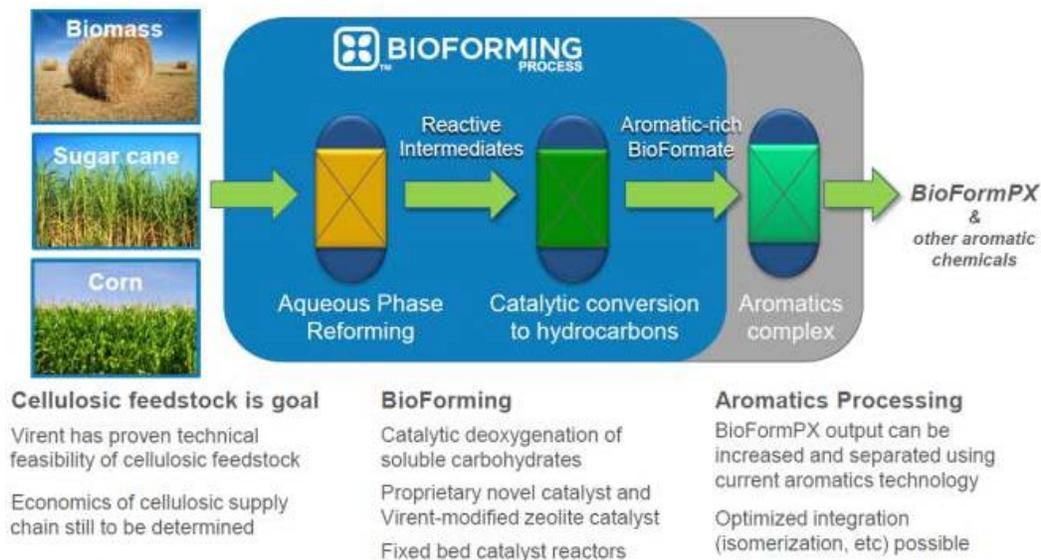


In 2013, Gevo completed its pilot plant to produce bio p-xylene (PX) and on May 29 this year announced its first sale to Toray. The PX was sold under a previously announced off take agreement with Toray. Toray also provided funding assistance for the construction of Gevo's PX demo plant at its biorefinery at South Hampton Resources, where Gevo also produces other hydrocarbon products such as renewable jet fuel and renewable iso-octane. Toray expects to produce fibers, yarns, and films from Gevo's PX, for scale-up evaluation and market development purposes.

Unlike Gevo, which is a fermentation process to produce the starting isobutanol, both Virent and Annelotech use a catalytic process.

## Virent Technology

Virent uses what is known as aqueous phase reforming in which mixed C5 and C6 sugars are converted to mixed hydrocarbons including p-xylene through a novel combination of Aqueous Phase Reforming (APR) technology with modified conventional catalytic processing. The APR technology was discovered at the University of Wisconsin in 2001 by Virent's co-founder and chief technology officer, Dr. Randy Cortright. The BioForming platform expands the utility of the APR process by combining APR with catalysts and reactor systems similar to those found in standard petroleum oil refineries and petrochemical complexes. A schematic of Virent's process is shown in Figure 23.



**Figure 23. Virent's Process for Bio P-Xylene.** Bioforming and aromatics separation for converting multiple feedstocks to high value hydrocarbons.

### Anellotech Process

Anellotech also uses a catalytic process but at much higher temperatures than Virent.<sup>87</sup>  
<sup>87</sup><http://www.sunycnse.com/download/Anellotech.pdf>

Anellotech's core technology, catalytic fast pyrolysis (CFP) for Biomass to Aromatics™, is based on scientific research performed in Professor George Huber's research laboratory at the University of Massachusetts-Amherst and on process and catalyst developments by Anellotech. A simplified schematic of this process is shown in Figure 24 below. The lignocellulosic biomass (i.e. wood waste, corn stover, sugar cane bagasse, or other non-food materials) is first dried and ground before injection into a fluidized bed reactor in the presence of a proprietary zeolite-based catalyst. In this one brief step, biomass is rapidly heated without oxygen and the resulting gases are immediately converted into desired aromatic and olefinic hydrocarbons along with CO, CO<sub>2</sub>, H<sub>2</sub>O, and undesired coke. The resulting benzene-toluene-xylene (BTX) mixture, which is identical to their petroleum-derived counterparts, fits easily into the existing petrochemical infrastructure and can be sold to petrochemical companies for processing in their existing separation units, or distilled and sold directly into the market.

On May 07, 2014 Anellotech announced it had begun production of 1kg quantities of BTX, available to support Anellotech's ongoing business development activities as well as strategic partners' downstream programs. No information has been provided as to their investors or strategic partners.

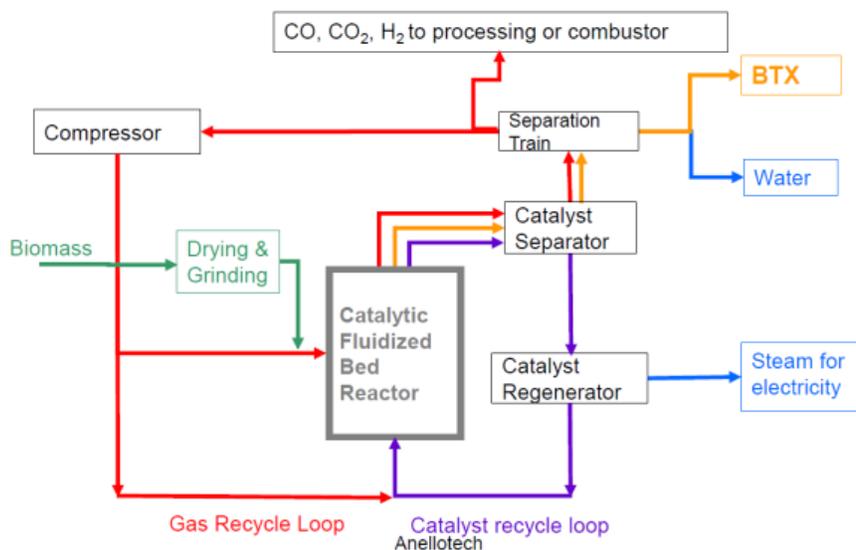


Figure 24. Anelotech Process for BTX Production. Figure modified from<sup>87</sup>.

### C 1.9 Acrylic Acid

The annual global market volume of acrylic acid was estimated at the end of 2011 at 4.1 million tonnes with a value of \$11bn at a growth rate of 4%/year<sup>88</sup>.

<sup>88</sup><http://greenchemicalsblog.com/2013/07/08/basf-cargill-novozymes-bio-acrylic-acid-milestone/>

Presently, acrylic acid is produced by the oxidation of propylene derived from the refining of crude oil. The major markets for acrylic acid and its derivatives include surface coatings, adhesives, plastic additives and co-monomers. Acrylic esters include methyl acrylate, butyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate and others. Acrylic acid is also used to produce polyacrylic acid or cross-linked polyacrylic acid compounds, which are used in the manufacture of super absorbent polymers. These polymers have wide range of applications in hygienic products, detergents, and waste water treatment chemicals. A breakdown of the acrylic acid market is shown in Figure 25.<sup>89</sup>

<sup>89</sup> Biobased chemicals conference, San Francisco, September 2012.

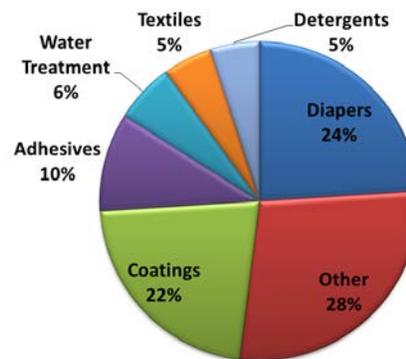


Figure 25. Breakdown of the Acrylic Acid Market. The existing global market is \$8 billion and growing with an interest in renewable alternatives. Figure modified from<sup>89</sup>.

Key players in the search to produce acrylic acid from renewable resources include the collaboration between Novozymes, Cargill and BASF and the Dow-OPXBio venture.

## Novozymes, Cargill and BASF

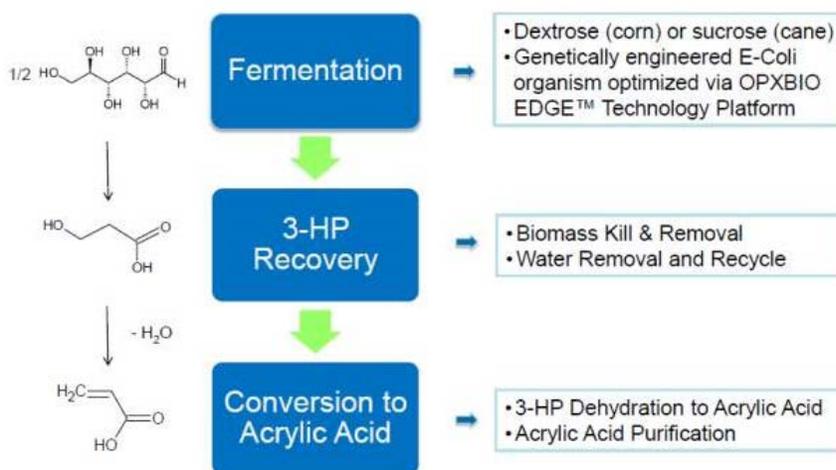
Novozymes and Cargill have collaborated on renewable acrylic acid technology since 2008. Both companies have worked to develop microorganisms that can efficiently convert renewable sugars into 3-hydroxypropionic acid (3-HP), which is the preferred precursor to acrylic acid. In August 2012, BASF announced it had now joined the collaboration. BASF is the world's largest producer of acrylic acid and has substantial capabilities in its production and downstream processing. The company plans initially to use the bio-based acrylic acid to manufacture superabsorbent polymers. The collaborative announced on July 3, 2013 that it was able to successfully produce 3-hydroxypropionic acid (3-HP) in pilot scale kilogram amounts.<sup>90</sup> The collaborative is looking to the next level of scale-up for the entire process in 2014 although no specifics on the capacity goal for biobased acrylic acid have been announced.

<sup>90</sup><http://greenchemicalsblog.com/2013/07/08/basf-cargill-novozymes-bio-acrylic-acid-milestone/>

## Dow-OPXBio

OPX Biotechnologies in partnership with Dow Chemicals is also working on bio acrylic acid and would currently seem to be ahead in the development of biobased acrylic acid. OPXBio noted in May 2013 at the Roquette Green Chemistry Symposium<sup>91</sup> that the company is within 80-90% of its commercial goals and is ready to start scaling up its 3,000 liter fermentation capacity to around 20,000-50,000 liters over the next 12 months.

<sup>91</sup>Roquette Green Chemistry Symposium May 2013.



**Figure 26. Schematic of OPXBio Route to Bio Acrylic Acid.** Figure modified from<sup>91</sup>.

It is not clear if this plant is yet on line. OPXBio also produces 3-HP as the intermediate chemical for bio acrylic acid. A schematic of their approach is shown in Figure 26.

Current and potential bioacrylic acid customers will dictate where the commercial plant will be built, according to OPXBio. The company said the acrylic acid market in general is growing faster in the Far East Asia and Latin America while North American growth is

just around 1%. OPXBio is already sending out their bioacrylic acid samples to their strategic lead customers for testing. The company said they can also sell their 3-HP but that is not their core strategy.

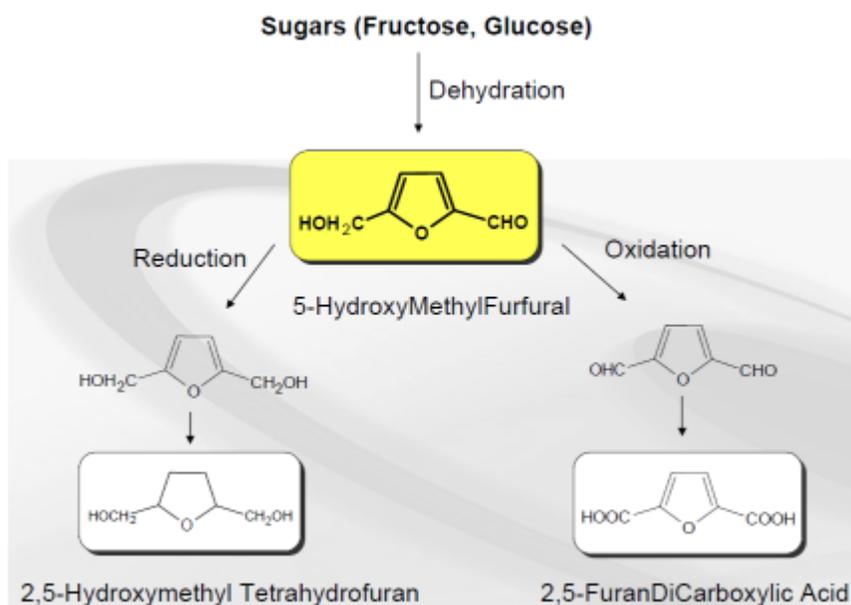
## C 2. New Monomers

### C 2.1 (2, 5 Furan dicarboxylic acid)-FDCA

2, 5-Furandicarboxylic acid (FDCA), also known as dehydromucic acid, is an oxidized furan derivative. This organic compound was first obtained by Fittig and Heinzelmann in 1876. However, little interest has been shown in this molecule until Avantium raised awareness as to its potential for production by catalytic degradation of glucose and in the future, cellulose. The primary product of their process is 5, hydroxy methyl furfural, which is converted to FDCA by oxidation as shown in Figure 27.<sup>92</sup>

<sup>92</sup><http://www.soci.org/News/Bioresources/~media/Files/Conference%20Downloads/2009/Bioplastic%20Processing%20Apr%2009/Jong.ashx>

Avantium is currently producing FDCA at its 40 tonnes/year pilot plant in Geleen, the Netherlands.

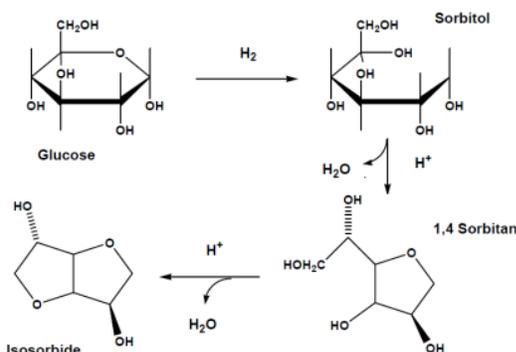


**Figure 27. Monomers Produced By Avantium.** Figure modified from<sup>92</sup>.

FDCA is a diacid and undergoes reactions typical for carboxylic acids (halogen substitution, ester and amide formation). It is being marketed by Avantium as a possible replacement of several petroleum based platform chemicals, e.g. terephthalic acid, adipic acid and other important di-acids. Today Avantium is focused on the use of FDCA as a replacement for terephthalic acid to produce a polyester known as poly ethylene furanoate (PEF) which they are targeting to displace PET based on its improved barrier properties. They are being helped by Coca Cola and others to bring the technology to market.

## C 2.2 Isosorbide

Isosorbide (1,4:3,6- dianhydro-D-glucitol) was first prepared by W. N. Haworth and L. F. Wiggins in 1948 by dehydrating D-sorbitol, which is obtained by reducing D-glucose. Isosorbide is one of the hexitol classes of bicyclic heterocycles derived from simple sugars such as dextrose. It is a cyclic crystalline product produced by the hydrogenation of dextrose to sorbitol followed by acid catalyzed dehydration: Figure 28.



**Figure 28. Chemical Conversion of Sorbitol to Isosorbide**

Initial interest in this monomer centered on the mononitrate derivative as an alternative to nitroglycerine for the treatment of angina. However, even in the 1960's interest was developing for isosorbide use in solvents, plasticizers and polymers. This interest has accelerated as industry increasingly turns its attention to renewable resource derived materials as alternatives to oil based products.

Isosorbide has two hydroxyl groups. Relative to the ring juncture, one is exo at the 2 position and the other is endo at the 5 position. The nature of the endo 5-hydroxyl group of isosorbide leads to internal hydrogen bonding between this particular hydroxyl group and the opposite ether ring oxygen. This increases the reactivity of the 5-endo position relative to the 2- exo position thereby creating the potential for differences in the reactions involving the hydroxyl groups with other species. However, during melt condensation reactions with isosorbide, operating under equilibrium conditions, generally both hydroxyls will react.

In 2002, the USDA–DOA Joint Biomass R&D provided the Iowa Corn Promotion Board (ICPB) a grant of \$700,000 to investigate the continuous isosorbide production from sorbitol using solid acid catalysis. The goal was to develop a renewable route to isosorbide using solid acid catalysts that was economically attractive. Yearly milestones were established over a three-year time period. The third year goal required pilot demonstrations of the technology and the development of economic models to determine if the catalyst system could perform economically and compete with conventional technology.

At the Greentech 2002 conference held in the Netherlands on April 25, 2002, Roquette, a French company founded in 1933, announced the starting of construction of a 0.15 million tonnes sorbitol unit in Lianyungang (Jiangsu), China. This plant would supposedly be on line in 2004. At the same conference they announced the results of their collaboration with Du Pont to produce polyethylene isosorbide terephthalate (PEIT). This

was claimed to provide a higher temperature performing modified PET with applications in hot fill containers, fibers and injection molded CD's. These findings are covered in US6656577 (B1), assigned to Du Pont, and issued December 02, 2003. However, this technology has not been commercialized. Isosorbide is now supplied commercially by ADM and Roquette.

#### **ADM isosorbide**

In 2010 Archer Daniels Midland (ADM) began selling isosorbide as a potential corn-based alternative to Bisphenol A (BPA) in plastics and other applications. Isosorbide can be used in polyesters for inks, toners, powder coatings, packaging and durable goods; polyurethanes for foams and coatings; polycarbonates for durable goods and optical media; epoxy resins for paints; and detergents, surfactants and additives for personal care.

#### **Roquette isosorbide**

In 2011, Roquette also announced that its production capacity of Isosorbide located in Lestrem (France) will attain several thousand tonnes by the beginning of 2011. Roquette markets isosorbide under the product trade name POLYSORB®. POLYSORB® is claimed to cost effectively replace fossil based diols for polymers synthesis. Its unique chemical structure can also bring outstanding properties of the new polymers. For instance, POLYSORB® can lead to new optical and thermal properties for new polycarbonate. Also, in PET markets, POLYSORB® enables the new PEIT to be used for hot fill containers. Another grade of isosorbide-POLYSORB® ID is sold as an alternative plasticizer to phthalates for PVC.

In January 2014, Mitsubishi Chemical Corporation announced the development of a new grade of high-performance, high-transparency bio-based engineering plastic called DURABIO™, using plant-derived isosorbide as its raw material. The new material features excellent optical properties and high resistance to heat and humidity.<sup>93</sup>

<sup>93</sup><http://www.m-kagaku.co.jp/english/newsreleases/2014/20140120-1.html>

Roquette is MCC's feedstock partner. The isosorbide is believed to replace all or some of the Bisphenol A used to produce polycarbonate. According to Mitsubishi Chemical, in contrast to easily breakable glass, transparent plastics such as impact-resistant polycarbonate are used for the front plate of automobile touch panels for safety purposes. The disadvantage of polycarbonates, however, is distortion in light transmission, which makes it difficult for users to see the touch panel, so a material that could overcome this problem has been eagerly awaited. MCC's new grade of DURABIO™ features excellent optical properties, and nearly eliminates distortion in light transmission, making it easy to see the touch panel surface.

Since autumn 2012, MCC has produced DURABIO™ at its Kurosaki Plant (Kitakyushu-shi, Fukuoka; General Manager: Nobuo Fukuda) with an annual production capacity of 4,500 tonnes. MCC says it will increase capacity for this product to 14,500 tonnes by 2015. However in 2013, according to IHS<sup>94</sup> a limited quantity of isosorbide polycarbonate—just 300 tonnes/yr, is currently being produced through this venture.

<sup>94</sup><http://press.ihs.com/press-release/bio-based-plastics/consumer-pressure-and-legislation-increasing-demand-and-development>

### C 2.3 Propane 1,3 diol (PDO)

PDO is used in the manufacture of polytetramethylene terephthalate (PTT), and thermoplastic urethane elastomers. A variety of chemical routes to propane 1,3 diol are known. For example, ethylene oxide may be converted to 1,3-propanediol over a catalyst in the presence of phosphine, water, carbon monoxide, hydrogen and an acid. This route was practiced by Shell Chemicals. An alternative route is the catalytic solution phase hydration of acrolein followed by reduction, or from compounds such as glycerol, reacted in the presence of carbon monoxide and hydrogen over catalysts having atoms from group VIII of the periodic table.

DuPont previously used the Degussa route of hydration of acrolein but in 2006 changed to producing PDO from corn dextrose by fermentation. During an initial research phase, scientists from Genencor and DuPont successfully combined DNA from three different microorganisms into one production strain and in doing so achieved greater than a 500-fold improvement in productivity. DuPont is producing corn-derived PDO at their commercial facility in Decatur, Ill. The economics of the process depends strongly on the yield of the fermentation process, the purification process, and on the cost of feedstock.

In March 2013, France-based METabolic Explorer announced that the company and its partner Malaysian biotech hub owner Bio-XCell are pushing ahead for their plans to construct a 50,000 tonnes/year biobased PDO facility in Bio-XCell's site in Iskandar. The facility is expected to have an initial output of 8,000 tonnes/year and uses crude glycerol as feedstock.<sup>95</sup>

<sup>95</sup>. <http://greenchemicalsblog.com/2013/03/18/bio-pdo-market-update/>

Finally, China-based consulting firm, CCM International, reported in January 2012 that Zhangjiagang Huamei Biomaterial Co., Ltd. was planning a 65,000 tonnes/year biobased PDO production plant in Changjiang River Chemical Industrial Park. There has not been any confirmation of this plant.

## SECTION 4. Present size of the Bioplastics Industry and projected growth trends.

Over the past few years there have been many studies claiming to define the present size of the bioplastics industry and projecting future growth trends. A summary of some of the major projections is provided in Table 14 below along with a synopsis of the various studies/comments later in the section. These studies indicate how confusing the actual picture is. There is a not a consistent picture presented. The only consistent theme among all the studies is that bioplastics growth will be in the double digits estimated to be between 16-29% CAGR. The highest growth projected will be in the non degradable plastics such as bio PE, bio PP and bio PET. PLA, starch blends and PHA's are still projected to show high growths but will lose market share to the non compostable bio plastics.

**Table 14**  
**Projection on Bioplastics Supply and Demand from Various Studies**

Study	Report Date	Projected Global Capacity End of Period (tonnes)	Projected Global Demand End of Period (Million tonnes)	Time Period Covered
Nova Institute	2013	12 million	12	2020
Eu. Bioplastics	2013	6.2 million	Not given	2017
Freedonia	2011		1.0	2015
World bioplastics	2009		0.9	2013
Freedonia	2008		0.816	2013
PR.Newswire	2010		0.138 *	2014
Eu Bioplastics	2007	1.36 million		2011
PROBIP	2009	2.94 million		2020
SRI	2010		0.281*	2014
SPE	2010		0.75	2014
BCC Research	2010		3.231	2015
PIRA			0.884 **	2015-2020

\*Biodegradable plastics only

\*\*Biodegradable packaging only

#### Review of the major market studies for Bioplastics.

##### (a) Nova Institute GmbH Study.<sup>96</sup>

<sup>96</sup> [www.nova-institute.eu](http://www.nova-institute.eu)

In March 2013, the Nova Institute GmbH published a study projecting that for Bio-based polymers production capacity will triple from 3.5 million tonnes in 2011 to nearly 12 million tonnes in 2020.

Bio-based drop-in PET and PE/PP polymers and the new polymers PLA and PHA show the fastest rates of market growth. The lion's share of capital investment is expected to take place in Asia and South America. The Nova-Institute carried out this study in collaboration with renowned international experts from the field of bio-based polymers. They claim it is the first time that a study has looked at every kind of bio-based polymer produced by 247 companies at 363 locations around the world and examines in detail 114 companies in 135 locations. According to this study, considerably higher production capacity was found than in previous studies. The 3.5 million tonnes in 2011 represents a share of 1.5% of an overall polymer production of 235 million tonnes in 2011.

The current producers of bio-based polymers estimate that production capacity will reach nearly 12 million tonnes by 2020. With an expected total polymer production of about 400 million tonnes in 2020, the bio-based share should increase from 1.5% in 2011 to 3% in 2020, meaning that bio-based production capacity will grow faster than overall production.

The most dynamic development is foreseen for drop-in biopolymers, which are chemically identical to their petrochemical counterparts but at least partially derived from biomass. This group is spearheaded by partly bio-based PET (Bio-PET) whose production capacity will reach about 5 million tonnes by the year 2020, using bioethanol from sugar cane. The second in this group are bio-based polyolefins like PE and PP, also based on bioethanol. Also “new in the market” compostable bio-based polymers such as PLA and PHA are also expected to at least quadruple the capacity between 2011 and 2020.

Most investment in new bio-based polymer capacities will take place in Asia and South America because of better access to feedstock and a favorable political framework. Europe’s share will decrease from 20% to 14% and North America’s share from 15% to 13%, whereas Asia’s will increase from 52% to 55% and South America’s from 13% to 18%. World market shares are not expected to shift dramatically, which means that every region of the world will experience development in the field of bio-based polymer production.

**(b) European Bioplastics Study.**<sup>97</sup>

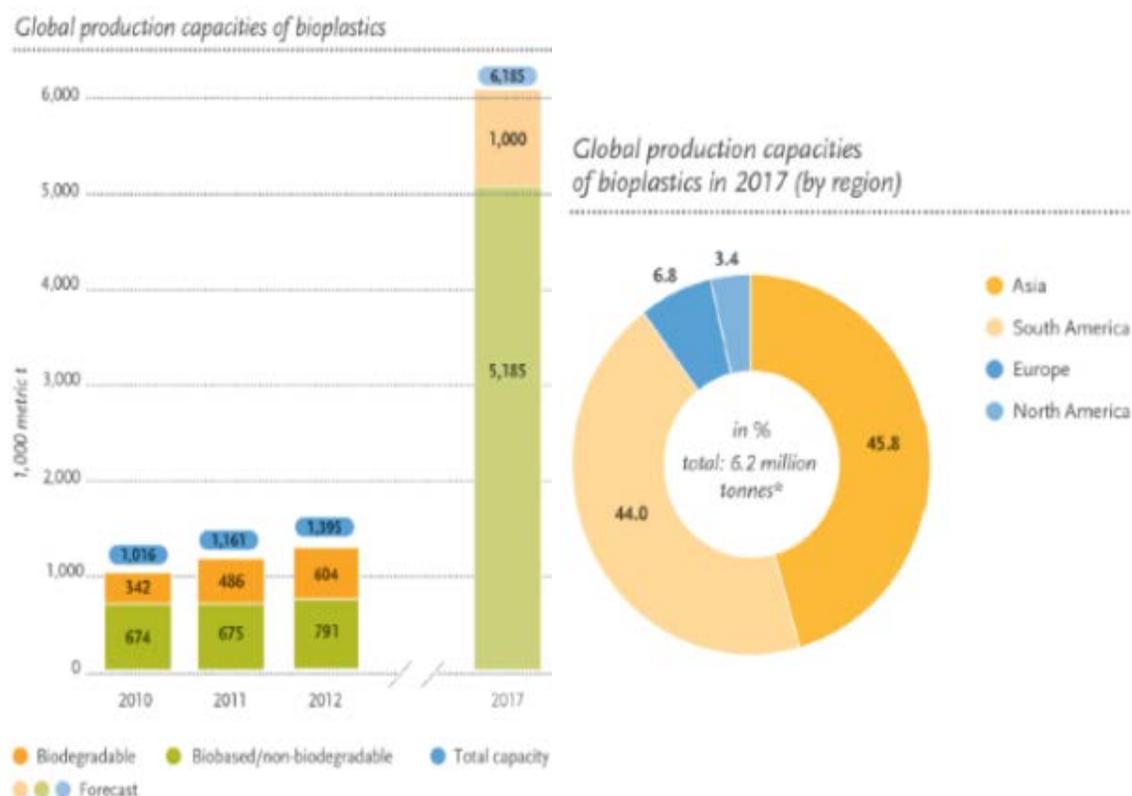
<sup>97</sup>[http://en.european-bioplastics.org/wp-content/uploads/2013/12/EuBP\\_market\\_data\\_2012.pdf](http://en.european-bioplastics.org/wp-content/uploads/2013/12/EuBP_market_data_2012.pdf)

The bioplastics market is predicted to grow from around 1.4 million tonnes (annual production capacity) in 2012 to approximately 6.2 million tonnes in 2017. By far the strongest gain is expected in the biobased, non-biodegradable bioplastics group.

Biobased versions of bulk plastics like PE and PET in particular are significantly increasing capacities. These so-called ‘drop-in’ solutions differ from their conventional counterparts only in terms of their renewable raw material base. Biodegradable plastics, which e.g. support biowaste collection and thereby increase waste stream efficiency, are also demonstrating impressive growth rates. Their production capacity will gain around 60 percent by 2017.

The packaging market will remain the leading segment for bioplastics applications. Here, the bioplastics industry offers a growing range of mature applications - much-needed new solutions that contribute to reducing the dependency on fossil feedstock, to minimizing the carbon footprint of packaging and that offer additional recovery and recycling options. While packaging is still the leading market segment, other very different segments are gaining in strength, in particular consumer electronics, automotive, and the fibre market. Projected global production capacities in the above study are presented in Table 15.

**Table 15. Projected Global Bioplastics Production Capacities.** Figure modified from<sup>97</sup>.



**(c) Freedonia Group.<sup>98</sup>**

<sup>98</sup><http://www.greenerpackage.com/bioplastics/world-demand-bioplastics-exceed-1-million-tons-2015>

Consumer preferences for sustainable materials, improved product performance, and price parity with petroleum-based plastics will be the key drivers in bioplastics growth. Projected Global demand for biodegradable and bio-based plastics will more than triple to more than 1 million tonnes in 2015, valued at \$2.9 billion-Table 16.

**Table 16. Projected Global Demand for Biodegradable and Bio- Based Plastics.** Table modified from<sup>98</sup>.

Region	Year			% Annual Growth	
	2005	2010	2015	2005-2010	2010-2015
North America	34	80	242	18.7	27.9
Western Europe	60	125	347	18.8	22.7
Asia/Pacific	33	83	320	20.3	31
Other Regions	3	12	116	32	57.4
<b>Total</b>	<b>130</b>	<b>300</b>	<b>1025</b>	<b>18.2</b>	<b>27.9</b>

According to this study, bioplastics have moved past the initial phase of market introduction and are now experiencing robust increases in demand in virtually all parts of the world. Gains will be fueled by a number of factors, including consumer preferences for environmentally sustainable materials, improved performance of bioplastic resins relative to traditional plastics, and the introduction of commodity plastics produced from bio-based sources. Ultimately, however, Freedonia notes that price considerations will be the primary determinant of bioplastic market success, and it is expected that rising petroleum costs will allow some bioplastic resins to be able to achieve price parity with conventional plastics by the end of the decade.

Biodegradable plastics accounted for 90% of the world bioplastics market in 2010. Excellent growth is forecast for the two leading biodegradable plastics—starch-based resins and polylactic acid (PLA)—both of which are expected to more than double in demand through 2015. The report adds that the fastest gains for biodegradable plastics, however, will be seen for polyhydroxy-alkanoate (PHA) resins, which are just entering the commercial market.

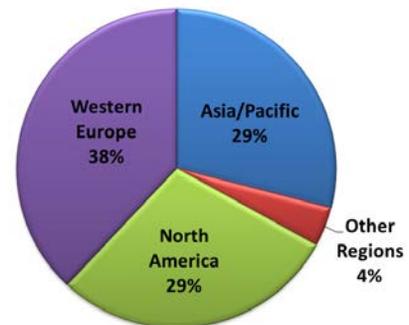
Despite the strong advances for biodegradables, nonbiodegradable bio-based resins will be the primary driver of bioplastics demand through 2015 and beyond. Gains will be fueled by the availability of commercial quantities of bio-based polyethylene from Braskem’s 200,000 tonnes/yr plant in Brazil, which opened in late 2010. Two other bio-based PE plants—as well as a bio-based polypropylene facility are also in the planning stages and are expected to open around 2015. Additionally, industrial production of fully bio-based PET is forecast to become a reality by the end of the decade. As a result, demand for non biodegradable bioplastics will rise from 30,000 tonnes in 2010 to 1.3 million tonnes in 2020.

**(d) World Bioplastics, November 2009 - World demand to rise more than fourfold by 2013.<sup>99</sup>**

<sup>99</sup>World Bioplastics The results of this study are illustrated in Figure 29.

Global demand for bioplastics, plastic resins that are biodegradable or derived from plant-based sources, will increase more than fourfold to 0.9 million tonnes in 2013, valued at \$2.6 billion. Growth will be fueled by a number of factors, including consumer demand for more environmentally-sustainable products, the development of bio-based feedstocks for commodity plastic resins, and increasing restrictions on the use of non-degradable plastic products, particularly plastic bags. Most important, however, will be the expected continuation of high crude oil and natural gas prices, which will allow bioplastics to become more cost-competitive with petroleum-based resins.

Non-biodegradable, plant-based plastics will be the primary driver of bioplastics demand, rising from just 23,000 tonnes in 2008 to nearly 600,000 tonnes in 2013. Biodegradable plastics, such as starch-based resins, polylactic acid (PLA) and degradable polyesters, accounted for the vast majority (nearly 90 percent) of bioplastics demand in 2008. Double-digit gains are expected to continue, fueled in part by the emergence on the commercial market of Polyhydroxyalkanoates (PHAs). PLA will also see strong advances in demand as new production capacity comes online, lowering the price of the resin and making it more widely available.



**Figure 29. Global Bioplastics Demand.** Global plastic demand in 2008 was 200,000 metric tons. Figure modified from<sup>99</sup>.

Western Europe was the largest regional market for bioplastics in 2008, accounting for about 40 percent of world demand. Bioplastics sales in the region benefit from strong consumer demand for biodegradable and plant-based products, a regulatory environment that favors bioplastics over petroleum resins, and an extensive infrastructure for composting.

Going forward, however, demand will grow more rapidly in the Asia/Pacific region, which will surpass the West European market by 2013. Gains will be stimulated by strong demand in Japan, which has focused intently on the replacement of petroleum based plastics. Other regions, such as Latin America and Eastern Europe, will see stellar gains in bioplastics demand from a very small 2008 base.

Currently, world bioplastics production is heavily concentrated in the developed countries of North America, Western Europe and Japan. This will change dramatically by 2013 when Brazil will become the world's leading producer of bioplastics. Furthermore, China plans to open over 100,000 tonnes of new bioplastics capacity by 2013, making that country a major player in the global industry.

**(e) August 2010 - US Degradable Plastics Market.**<sup>100</sup>

<sup>100</sup>. [PRnewswire.com](http://PRnewswire.com) US demand to rise nearly 11% annually through 2014.

Demand for degradable plastics in the US is projected to rise nearly eleven percent annually to 0.138 million tonnes in 2014, valued at \$390 million. Although representing less than one-half of one percent of all thermoplastic resin demand in 2009, degradable plastics will exhibit substantial growth opportunities. Degradable plastic advances will be fostered by their increased cost competitiveness with petroleum-based materials, as well as their sustainability and more benign environmental profile. Degradable plastics demand is being broadened by enhanced performance properties brought about by more sophisticated polymerization and blending techniques. Testing and certification standards have also been established for many types of biodegradable plastics, with growing pressures to limit packaging waste and expand the composting infrastructure.

Poly(lactic acid) (PLA) will grow at the fastest pace through 2014, driven by a more competitive price structure and greater availability. Myriad opportunities are expected, particularly in fiber applications such as nonwovens. Starch based plastics will have a good outlook as a result of improved resin blends and applications in such areas as compostable yard and kitchen bags, in addition to food service items such as plates, bowls and cutlery. Demand for Polyhydroxyalkanoates (PHAs) will more than double, driven by an increase in the availability of PHA plastics and products. Opportunities are expected in areas such as films and molded containers. Slower growth is expected for photodegradable films such as ring carriers due to a maturing beverage container segment and competition from shrink film and paperboard packaging.

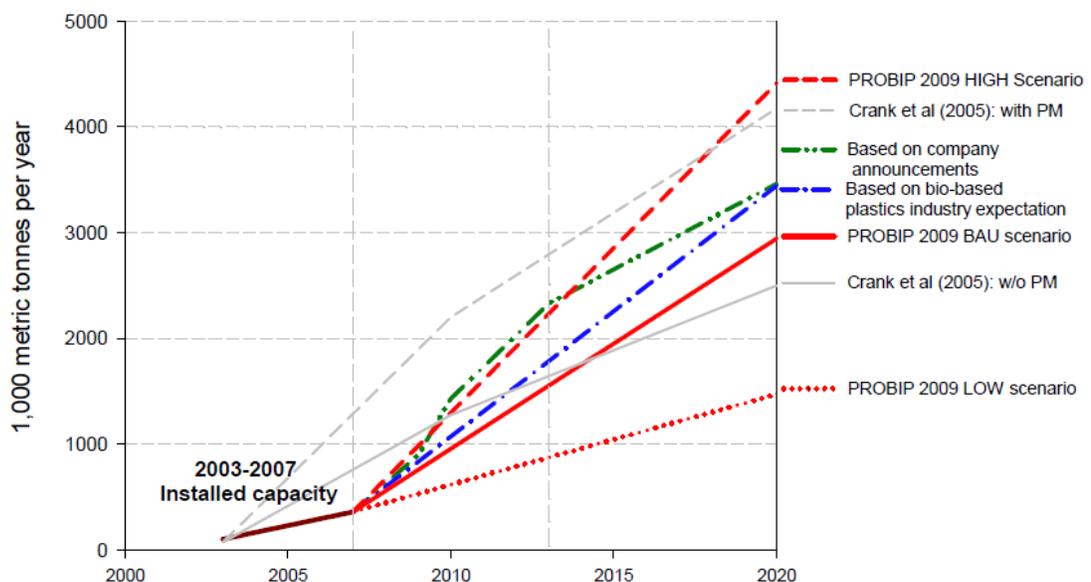
Packaging, which accounted for nearly three-quarters of all degradable plastic in 2009, will exhibit good growth through 2014 in film and molded containers. However, most rapid growth is expected for non packaging products, particularly textile fibers in areas such as nonwovens, bedding and apparel. Other degradable non packaging products include compost bags, foodservice disposables and agricultural mulch.

**(f) June 2009 -Product Overview and Market Projection of Emerging Bio Based Plastics. (PRO-BIP 2009)<sup>101</sup>**

<sup>101</sup>. [www.plastice.org/fileadmin/files/PROBIP2009\\_Final\\_June\\_2009.pdf](http://www.plastice.org/fileadmin/files/PROBIP2009_Final_June_2009.pdf)

This is by far the most detailed and optimistic study published to date on Bioplastics Capacity Projections. Based on what are stated to be industry expectations the projected bioplastics capacity in 2013 is expected to be approximately 2.3 million tonnes rising to 2.94 million tonnes by 2020 under the business as usual scenario (BAU) scenario. Various projections from optimistic (all capacity announcements are implemented to low (very pessimistic projection).

This study claims a “technical” substitution potential that bio polymers can replace 90% of all existing polymers if economic barriers, technical challenges in scale up and the short term availability of feedstocks plus the need for the plastics conversion sector to adapt to new plastics can all be overcome. Projections from this study are shown in Figure 30.



**Figure 30. PRO-BIP 2009 Study Projections for Bioplastics Growth.** Figure modified from<sup>101</sup>.

**(g) January 2010 CEH Marketing Research Report.<sup>102</sup>**

<sup>102</sup>. [SRIconsulting.com](http://SRIconsulting.com)

In 2009, demand for biodegradable polymers in North America, Europe and Asia accounted for most of the global consumption. Despite the economic crisis which hit the chemical and plastics industry, the market for biodegradable polymers grew in 2009 in almost all regions. In Europe, the largest global market growth was in the range of 5–10% (depending on products and applications, compared with 2008). Total consumption of biodegradable polymers in these three regions is forecast to grow at an average annual rate of nearly 13% over the five-year period from 2009 to 2014. The food packaging, dishes and cutlery market is the single largest end use and will be the major growth driver in the future.

Europe continues to be the largest biodegradable polymers consuming region, with about half of the global total. Major market drivers for biodegradable polymers in this region include legislation, depleting landfill capacities, pressure from retailers, growing consumer interest in

sustainable plastic solutions, fossil oil and gas independence, and the reduction of greenhouse gas emissions.

### **Comments on the above projections:**

#### **Capacity Assessments**

Four of the published studies project actual manufacturing capacities for bioplastics all of which are European studies and are based on two factors:

- Announced company capacity plans.
- Projected plant capacities based on perceived growth.

The Nova Institute study is very aggressive on forecasted capacities for the non biodegradable plastics. The PRO BIP 2009<sup>101</sup> study, which was commissioned by European Polysaccharide Network of Excellence (EPNOE) and European Bioplastics, provides several scenarios.

The information presented in this particular study is based on the author's assertion that these figures represent a total technical substitution potential for conventional plastics. However, they do conclude this will not occur in the short-to-medium term due to economic barriers, technical challenges in scale up and short term availability in feed stocks. Little mention is made of performance issues with bioplastics, which is surprising. The figures are also based on announcements from potential and existing suppliers. In reality, some of these announcements have either not been validated or companies have delayed. For example, in the case of the Dow/Crystalsev Joint Venture and the subsequent Dow-Mitsui JV, activities for bio Polyethylene have been completely abandoned.

It is obvious that the projections of Fredonia, SPE, and BCC Research for all bioplastics demand are widely different. In particular, the BCC figures are, in the opinion of Jim Lunt & Associates LLC, extremely difficult to align with reality. Even the PRO-BIB study puts capacity in 2015 well below the 2015 projections for demand by BCC. In 2015, BCC projects the global demand for bioplastics to be 3.21 million tonnes. This is obviously grossly inflated given who the known suppliers are today.

Why do all these studies differ so widely? It is clear that these types of studies often rely on marketing hype. Some have no real knowledge of the companies or what the realistic market penetrations are. Many rely on interviews with company marketing personnel who exaggerate their sales to project their business to the marketplace. Many quote expected capacity while others predict expected demand. It is the opinion of Jim Lunt & Associates LLC., that the biggest confusion is in identifying what is being included under Bioplastics. Even those studies that discuss only "Biodegradable Plastics" or "Biodegradable Packaging" are divergent and difficult to rationalize. There is obviously a need to bring a different perspective to these trends, one based on intimate knowledge of the players, markets and technologies.

### Jim Lunt & Associates Assessment:

Based on discussions with key players and knowledge of the marketplace the estimated capacities and sales in 2013 for the major bioplastics are shown in Table 17.

**Table 17. Estimated manufacturing capacities and sales for 2013.**

Product	2013 Bioplastics Manufacturing Capacity (million tonnes)	2013 Sales Estimates (million tonnes)
“Green” Polyethylene	0.12	0.06
Bio PET	0.66*	0.66*
PLA	0.26	0.2
Starch Blends	0.2	0.15
PHA’s	0.02	0.005
Others	0.05	0.02
Totals	1.31	1.095

\* Contains only 30% renewable resource based on bio ethylene glycol.

Clearly the capacity estimates and actual sales are both significantly lower than those found in the EU market studies and more in line with the Fredonia and World Bioplastics studies. The actual 2013 capacity is close to the 2011 capacity projected by European Bioplastics before inclusion of the developing non-biodegradable plastics. PHA suppliers are still struggling with high price and the only present domestic supplier, Metabolix, no longer has a dedicated production plant.

Meredian is claiming it can produce its PHA at around \$2.20/kg but as yet the product is not in the marketplace. In addition, Cereplast has declared bankruptcy. Product sales are approaching plant capacities in the case of bio PET (based on MEG supply), PLA and starch blends. For green PE it remains to be seen how the supply of cheap natural gas will ultimately affect this initiative.

CAGR for bioplastics, which is believed to be around 19% overall for the foreseeable future, will probably be less than expected for bio polyethylene due to the natural gas dynamic. Bio PET will increase as the JBF bio MEG plant comes on stream. PLA and starch products will still show significant growth but will begin the mature beyond 2015 as the accessible single-use compostable market becomes saturated.

The overall future of the bioplastics industry will be driven by the success of replacing the petrochemical monomer base by renewable based analogues. One factor not being considered by these studies, is if natural gas become the dominant energy source in the USA then C3 and C4 aliphatic molecules plus aromatics such as terephthalic acid, benzene, toluene, xylenes and all their downstream derivatives will become in short supply. This will drive the development of the furanics such as FDCA and bio routes to the aromatics such as those being developed by Gevo, Virent and Anellotech.

In summary, capacity projections for Bioplastics are, in general, over stated due to announced capacities being delayed and overoptimistic growth scenarios. Growth of today’s bioplastics is still limited by infrastructure and performance issues against incumbents and, in some cases, by pricing. While oil prices are projected to remain at a level  $\geq$  \$90/barrel in the timescale of this study, such

increases will not allow more rapid penetration of today's major products without improved performance. Single-use compostable markets will continue to grow but at slower rate than projected due to lack of infrastructure for disposal.

New entrants such as polyethylene from sugar cane appeared to open the pathway to compete in markets dominated by conventional polymers with known manufacturing processes and performance. This trend with expansion to other olefins may be inhibited by the emerging natural gas supply. Intense activity in other bio monomers will probably be first observed in the manufacture of poly butylene succinate, followed by other known polymers. Speed for growth of these materials will depend on economics and the ability for the products to be recovered and recycled. One other factor affecting ultimate growth is how readily the technologies can be developed to cost effectively produce product from non-edible feedstocks such as wood pulp, waste fibers and other materials.

There is no doubt that bioplastics are here to stay, however, how many of these bio routes to new and existing materials will really be successful is still an open question. Prices for bioplastics are not projected to deviate significantly from today's pricing although some upward movement may be allowed as petrochemical pricing increases with oil going to \$90/barrel and possibly higher.

## **SECTION 5. Legislative activities and policies driving adoption of bioplastics.**

The last few years have seen worldwide, a growing number of governments developing a strategy and policy framework to support the development of a sustainable and competitive bioeconomy. Several of these policies offer generic support for the further development of biochemicals, biomaterials and bioplastics, promoting bio-based products or the bio economy in general. Most of them focus on research and innovation. Many countries have implemented policies banning single use plastics bags. However, only a few countries have developed a specific set of policies targeting the development of bioplastics. An excellent review of the various incentives, much of which has been used in this section, is provided in the report below.<sup>103</sup>

<sup>103</sup>.<http://www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?cote=DSTI/STP/BIO%282013%296/FINAL&docLanguage=En>

### **Brazil**

Bioplastics production in Brazil is very attractive due to its cost competitiveness and positive demand drivers, such as increased consumer interest in environmentally friendly packaging and a greater emphasis on sustainability on the part of product manufacturers worldwide.

In February 2012, the Brazilian Agriculture Ministry released a Strategic Plan for the sugar-energy industry, including a series of measures involving credit and financing via government funds, available to the sugarcane industry at market rates. In a related move, in January 2012, the Brazilian development arm, BNDES, created a new program to encourage the production of sugarcane by financing the renovation of old sugarcane farms and the expansion of the cultivated area, with a budget of BRL 4 billion (approximately USD 1.75 billion).

The government of Brazil launched a growth acceleration program in 2007 and spent over USD 220 billion through 2010 on infrastructure, funded by the federal government and by state-owned and privately owned companies. In 2010, the project was continued with a second phase promising USD 526 billion from 2011 to 2014 and USD 346 billion after 2014 to improvements in energy, transportation, urban infrastructure, housing, sanitation, electricity and social programs. While the program is designed for the whole economy and not just the bioplastics industry, it is expected to drive the growth of the bioplastics industry. The Institute for Technological Research (IPT) a public organization supported by the State of São Paulo is one of Brazil's largest research institutes. Part of this institute, The Laboratory of Industrial Biotechnology (LIB), works to develop new polymers based on renewable resources. Current work includes increasing the scale of bioreactors, using enzymes and solvents to extract and purify biopolymers, characterizing biopolymers, and developing polymers for controlled delivery of active pharmaceutical ingredients.

### **China**

China recently included the bioeconomy as a priority within its 12th Five-Year Plan for Energy Saving and Emission Reduction, aiming to transform the mode of economic development, establish an energy saving and environmentally friendly society and strengthen the capacity of sustainable development. During the coming five years, China has pledged to invest more than USD 316 billion in promoting energy-saving and low-carbon projects across the country. Also stressed in the Plan is the need to accelerate China's bioeconomy to serve major needs in health, agriculture and environmental protection. For the first time in a five-year plan, China has also set a target for the reduction of carbon intensity, which could also affect the plastics sector (MEP, 2012).

Biodegradable plastics receive substantial political and research support in China. The National Development and Reform Commission has set up a biomass special equity fund, and institutions such as the Institutes of Physics and Chemistry of the Chinese Academy of Sciences, Tsinghua University, and Sichuan University are actively engaged in research. China has also encouraged the development of polylactic acid (PLA) materials. Support for bio-based chemicals includes numerous incentives for producers and a preferential tax treatment for selected firms in emerging biochemical industries. In addition, since 2005, a specific program promotes production and consumption of biodegradable plastics.

### **France**

In 2005, the French General Directorate for Competitiveness, Industry and Services created the so called Competitiveness Clusters. These bring together companies, research centers and educational institutions in order to develop synergies and co-operative efforts, including some relevant to the bioeconomy. The French Government complements cluster development by allocating financial support to the best research and development and innovation platform initiatives. One of the clusters is the 'Industries and Agro-Resources' Cluster or IAR. This cluster unites stakeholders from research, higher education, industry and agriculture in the Champagne-Ardenne and Picardy regions of France around a shared goal, the value-added non-food exploitation of plant biomass. In order to achieve this ambitious objective, the IAR cluster has defined four strategic fields of activity around the biorefinery concept: bioenergy, biomaterials, biomolecules and green ingredients. A large number of international-scale research and development projects have already been launched covering the four target markets and there are also links to international clusters in countries including Canada, Finland and Hungary.

Toulouse White Biotechnology (TWB) is a Public Private Partnership (PPP), that was created in 2011, granted by the French National Agency for Research the level of EUR 20 million over 10 years. Its mission is to design and build the biological tools (e.g. enzymes and microorganisms) required for the novel production of biofuels, biopolymers and biomaterials using renewable carbon, to contribute to the development of the bio-based economy. The thrust of TWB is to use the PPP for advancement from research to pre-industrial demonstrator, founded upon 20 private companies, 5 investors and 9 public partners and local authorities. A novel aspect of TWB is the Bio-Ethic Evaluation Platform, which examines the social acceptance of products and processes

### **Germany**

The Bioeconomy Research and Technology Council (BÖR, BioÖkonomieRat) is funded jointly by the Ministry of Education and Research and the Ministry of Food, Agriculture and Consumer Protection. It is an independent advisory body to the German government for all matters relating to the bioeconomy. The Council is made up of experts from university and non-university research institutes, from the federal government's own departmental research sector and from research in the private sector.

The mission of the Bioeconomy Council is to accelerate the development of innovative technologies and identify the need for future research. Another task of the Council is to analyze the strategic goals of Germany as a whole, and its individual Regions. The BioEconomy Council's first term has been set at three years and is supported by an office in Berlin.

The aims of the BioEconomy Council are:

- To offer an overview of the opportunities and prospects of the bio-economy in Germany.
- To deliver scientifically-based recommendations for measures to deliver sustainable solutions to global challenges.
- To develop a supportive environment for research, education and training, and student support.
- To help strengthen networks of relevant actors from science, business and politics with a view to achieving maximum harmonization on strategic questions.

In 2010, the Council published the *Bio-economy Innovation Report* (BÖR, 2010) placing emphasis on increasing biomass yield volumes and more efficient production processes in the food and energy sectors.

Germany has also developed an “*Action plan for the industrial use of renewable raw materials*” (BMELV, 2009). In 2007, the German Federal Ministry of Education and Research initiated the creation of five German regional industrial biotechnology clusters. Among these clusters is CLIB2021 (co-founded with the Ministry of Innovation, Science and Research of the German State of North Rhine-Westphalia) with 32 founding members. Since then the cluster has grown to include more than 70 academic institutions, companies and investors, has launched research and development projects with a total volume of EUR 50 million, has founded 5 start-ups and 10% of its members are international. Another cluster is Biom Wb with two demonstration plants for cellulosic ethanol and acetic acid, a new multi-purpose pilot plant and a degree program in industrial biotechnology at the Technical University of Munich.

### **Italy**

In 2013, Italy banned the distribution of traditional plastic carrier bags, allowing only the commercialization of biodegradable single use and long-life reusable bags. Some of the positive effects of this initiative include:

- New capacity of biodegradable polyesters of more than 200 000 tonnes in Europe.
- New plants and projects under development/construction in Italy with high investment from private companies. In Italy two chemical sites have been converted in Lazio and Umbria.
- Two new fermentation plants in Piedmont (bio-succinic acid) and Veneto (bio-BDO) and an integrated biorefinery in Sardinia are under construction (about EUR 700 million is expected to be invested between 2012-2015 in research and development and pilot and demonstration plants in the field of bio-based products).
- Matrica JV (Novamont-ENI) for the creation of a large green chemistry hub in Europe: 50/50 J-V between Polimeri Europa/ENI and Novamont for the transformation of the Porto Torres chemical site of ENI into a third generation biorefinery for the production of bioplastics, biolubricants and biofillers/additives for low rolling resistance rubber. The biorefinery will directly employ about 680 people with significant indirect and direct effects on the local areas.
- Production of biopolymers in the carrier bags sector increased from 8% in 2010 to 28% in 2011. The sector is hence strengthening its role and contribution to the achievement of a strong

bioeconomy in Italy all along the value chain. Moreover, revenues for the carrier bags sector increased from EUR 674 million in 2010 to EUR 732 million in 2011 (data from Plastic Consult and a study commissioned by Assobioplastiche, the Italian Association for Biodegradable and Compostable Plastics).

- In 2011, start-up of first dedicated cultivations by SINCRO (a joint venture between Novamont and a cooperative of 600 farmers of the COLDIRETTI Association) in Umbria for biolubricants in agriculture and by Novamont in Sardinia to feed the Matrica biorefinery.

Another significant effect of the policy of banning conventional plastic bags in favor of compostable products is that Italian citizens were induced to adopt behavior that has a positive impact on environmental sustainability. Recent estimates show that 94% of Italian citizens believe that the law is an important milestone and step towards environmental improvement (ISPO, 2011). The law has helped to build widespread citizen awareness of the need to protect the natural environment and the fundamental role played by innovation in this respect. Estimates show that 88% of Italian citizens recognize that biodegradable and compostable plastics are a key innovation capable of triggering multiple positive effects (ISPO, 2011).

Since the launch of the European Union Bioeconomy Strategy, the Minister of Economic Development in Italy has set up a working group on green chemistry with the aim of elaborating a strategy at a national level. In May 2012, the Ministry of Education, Universities and Research launched a call for implementing clusters focused on top innovative sectors for the country, one of them being green chemistry. The cluster currently has 114 members (public and private), including the Italian Federation of Chemical Industries. It has about EUR 50 million of public and private funds addressing the finance of parallel, complementary three year R&D projects along with training projects for Masters students, PhD students and young scientists in the area of green and sustainable chemistry, biomaterials and industrial biotechnology. Furthermore, it will have the responsibility to develop the strategic R&D agenda and the implementation action plan on a bio-based economy for Italy.

## Japan

Following the ratification by the Japanese Government of the Kyoto Protocol in June 2002, the Government announced (December 2002) two measures: the *Biotechnology Strategic Scheme* and the *Biomass Nippon Strategy*. The main objective of the two measures was to promote the utilization of biomass to reduce the consumption of fossil resources and to mitigate global warming through the use of biotechnology. The policy objective stated in the *Biotechnology Strategic Scheme* is to replace approximately 20% (2.3 to 2.7 million tonnes per year) of conventional plastics with plastics from renewable resources by 2020. The *Biomass Nippon Strategy* was revised in March 2006 to accelerate the growth of biomass towns and to promote the utilization of biofuels.

The *Biomass Nippon Strategy* has prompted companies such as Toyota and NEC to accelerate their levels of research and development into bio-based plastics and to raise the bio-based content of their products. Japanese vehicle manufacturer Toyota is planning to switch 20% of the plastics used in its vehicles to bio-sourced plastics by 2015 and expects bioplastics to help in its efforts to accomplish its company-wide goal of reductions in CO<sub>2</sub> emissions.

To help to develop the market for bioplastics, the Japan BioPlastics Association (JBPA) started a certification program for products containing biomass-based plastic content. The association has

established standards as well as a methodology for the analysis and the evaluation of these plastics. The program includes a logo easily recognizable by consumers. The JBPA certification, called BiomassPla, specifies that products with the logo must contain 25% bio-based plastic by weight. So far, JBPA has certified about 900 biodegradable plastic products in Japan. The system is based on a positive list system for all components, biodegradability specifications based in Japanese Industrial Standards, safety certification of all components and proof of no hazardous effects to soil.

### **Korea**

In 2012, the Korean government announced a “Strategy for promotion of industrial biotechnology”, with the goal of establishing a mid-to long-term strategy to develop related technology and devise detailed measures for implementation, contributing to lowering the existing dependence of the economy on crude oil. By 2020, this effort is expected to result in replacing 4.8% of crude oil imports with biochemical product manufacturing, reducing carbon dioxide emissions by approximately 10.8%, and generating at least 43,000 new jobs.

Several companies have made the decision to use biobased materials in their product lines. Samsung Electronics has produced a mobile phone that uses a bio-based material externally. LG Hausys has produced flooring and wallpaper that uses PLA material. Furthermore, SK Chemical has produced a heat resistant bioplastic product, and Hyundai Motors plans to replace interior material partially in their new models with bio-based material.

The Korea Bioplastics Association (KBPA) has established an authentication program for products made of, or based on, biomass in order to expand the understanding of bioplastics and promote supply. KBPA’s authentication system is called “BiomassPlastic Certification”, and can be attained only when more than 25% of a product consists of biomass-derived ingredients. The Korea Biomaterial Packaging Association (KBMP) is also operating a bioplastic certification scheme. The Korean government is recommending that these two programs be united. Furthermore, the government has a plan to review a preferred procurement system for public institutions for authenticated products, and the establishment of an insurance system for trade in order to expand exports.

Some research programs are now in progress supported by the government: The development of technology for manufacturing of biomass-based C3 platform compounds; the development of technology for production of heat resistant bioplastic; the development of technology for production of 2,3-butanediol and derivatives; and the development of materials using woody biomass-based polymers. In addition, the government plans to implement the “Industrial Biotech 2.0: Green Carbon Korea Project” from 2014, investing around KRW 250 billion (approximately USD 222 Billion) for 5 years. The purpose of this project is to create a green carbon-based industrial biotechnology in Korea, and to reduce the crude oil dependence of the five core industries (electric/electronic, automobile, petrochemical/refinery, textiles and industrial materials).

### **Malaysia**

The Malaysian Government recently announced a new Bioeconomy Initiative Malaysia (BIM), a comprehensive plan to encourage commercialization in the biotechnology industry. Endorsed by Malaysia’s Biotechnology Implementation Council and launched by the Prime Minister of Malaysia in November 2011, BIM is the framework for the nation to develop a high-income bioeconomy through a sustainable ecosystem of research and development and commercialization in the areas of agriculture, healthcare and industrial biotechnology by 2020. Action areas include: medical

biotechnology, including production of vaccines, medical devices and biopharmaceuticals; industrial biotechnology, including energy and bio-based chemicals; and agricultural biotechnology.

The Malaysian Government expects that the Bioeconomy Initiative will generate around 20,000 job opportunities by 2020 in the entire biotechnology ecosystem and related value chain. A complementary policy, the National Biomass Strategy 2020, outlines how Malaysia can develop new biomass sectors with the aim of creating higher value-added economic activities that can contribute towards gross national income and create skilled jobs

### **Netherlands**

In the Netherlands, the Cabinet of Economic Affairs, Agriculture and Innovation has decided that the bio-based economy is one of the emerging economic pillars to be supported. The development of the national strategy was the result of an on-going interaction between business, society and science, stimulated by policymakers. In April 2012, the Cabinet presented a mid- and long-term vision and strategy for the bio-based economy. The “innovation contract bio-based economy” is a joint agenda developed by industry and research organizations. It contains six work packages, each covering the entire innovation chain (from more basic research to valorization). ‘Bio-based materials’ is one of the work packages. In total, more than 100 companies will participate in the projects and have committed more than EUR 200 million.

BE-Basic<sup>34</sup> (Bio-based Ecologically Balanced Sustainable Industrial Chemistry) is a public-private partnership (PPP) that develops industrial bio-based solutions for a sustainable society and has a research and development budget of more than EUR 120 million. Half of this is funded by the Ministry of Economic Affairs, Agriculture and Innovation. BE-Basic was founded early in 2010 and maintains an international focus via strategic partnerships with a select number of countries: Brazil, Malaysia, United States and Vietnam.

### **Norway**

A Norwegian Industrial Biotech Network was set up in mid-2012. Its main objective is to stimulate innovation through partnerships and dissemination of knowledge. The network will connect academia and industry across research disciplines, industry sectors and geography. The network is the result of a joint initiative by Innovation Norway, the Research Council of Norway and SIVA (Industrial Biotech Network Norway, 2012).

In February 2011, a memorandum of understanding was signed between Innovation Norway and the Technology Strategy Board in the United Kingdom. This collaboration agreement aims to foster transnational collaboration between industries and research institutions in the area of industrial biotechnology and biorefining. In 2012, it was decided to work together to support nine new research and development projects to create innovative processes to generate high-value chemicals through industrial biotechnology and biorefining. The United Kingdom Technology Strategy Board has offered grant funding totaling GBP 1.82 million to the nine United Kingdom-led projects (four full-scale collaborative research and development projects and five feasibility projects) and four of these will also be supported by Innovation Norway, which is providing additional funding of GBP 400 000 to the Norwegian businesses that are taking part. The projects will look at how industrial biotechnology and/or biorefining can be competitively applied to the production of high value chemicals and will see collaboration between industrial biotechnology developers, higher education institutions and the chemicals sector.

## **Sweden**

In February 2012, the Swedish Government prepared a “Swedish Research and Innovation Strategy for a Bio-based Economy” (FORMAS, 2012). The following research and development needs were defined:

- The replacement of fossil-based raw materials with bio-based raw materials;
- Smarter products and smarter use of raw materials;
- Change in consumption habits and attitude;
- Prioritization and choice of measures (e.g. environmental consequences, socio-economic consequences and governing policies).

## **Thailand**

Thailand is a biomass-rich country with abundant feedstock resources and more than 4000 companies in the plastics industry. Since 2006, the Thai Government has declared the bioplastics industry to be one of the strategic industries that the Government is promoting in its drive towards sustainable growth and development. This resulted in 2008 in a National Roadmap for the Development of Bioplastics Industry, developed by the National Innovation Agency (Ministry of Science and Technology).

This action plan for 2008-2012 was focused on four main strategic areas:

- Sufficient supply of biomass feedstock.
- Accelerating technology development and technology co-operation.
- Building industry and innovative businesses.
- The establishment of supportive infrastructure.

The strategies covered the entire value chain of the bioplastics industry. The roadmap provided targets, indicators and action plans and designated sectors and organizations for implementation. The total budget for the roadmap strategies at that time was USD 60 million.

Examples of incentives for investment in bioplastics included:

- A corporate income tax exemption for eight years and additional 50% reduction for five years.
- Deductions for infrastructure construction and installation costs.
- Import duty reductions or exemptions for machinery and raw materials.
- Permission to bring in foreign experts and technicians.

These government initiatives and incentives have led to several investments in production facilities by both international and domestic firms. The Thai Government has also encouraged Thai companies to engage with international bioplastics companies and has promoted close collaboration with international partners. In addition to investment incentives, other government policies have promoted the use of bioplastics and the development of Thai industrial standards for bioplastics and consumer awareness.

More recently, the Thai Cabinet has approved additional supportive measures to boost investments in this sector, such as a USD 10 million grant for the construction of a pilot bioplastic resin production facility. The rest of the investment is to come from the local private sector, and the facility was to become operable by 2013. In addition to the pilot plant construction, supportive measures to enhance commercial investments in the local bioplastics industry over the period 2011-2015 will target five areas:

- Biomass availability.
- Bioplastics research and development.
- Standardization system.
- Business and investment privileges.
- Market promotion and environmental management.

A total of USD 20 million has been committed by the Thai Government to support the implementation of these supporting measures in the five areas. It is expected that development of the local bioplastics industry will take place in accordance with the National Roadmap.

### **United Kingdom**

In the United Kingdom, the Technology Strategy Board has created an Industrial Biotechnology Special Interest Group (IB-SIG) to operate across its networks to implement the recommendations of the 2009 Industrial Biotechnology Innovation and Growth Team (IB-IGT, 2009). Also in the United Kingdom, the Integrated Biorefining Research and Technology Club (IBTI Club) was launched in 2009. This group consists of a research and technology partnership involving the Biotechnology and Biological Sciences Research Council (BBSRC), the Engineering and Physical Sciences Research Council (EPSRC), the Bioscience for Business Knowledge Transfer Network (KTN) and industry. The club will interface with the KTN's wider Integrated Biorefinery Technologies Initiative (IBTI) and will invest around GBP 6 million in industrially relevant, innovative, basic biological, chemical and engineering research in biorefining technologies.

### **United States**

In April 2012, the Obama administration announced a broad plan to foster development of the Bioeconomy, *The National Bioeconomy Blueprint*, including the use of renewable resources and biological manufacturing methods. The blueprint is aimed at fostering all biology-based businesses, including pharmaceuticals and medical devices.

The *National Bioeconomy Blueprint* describes five strategic objectives for a bioeconomy with the potential to generate economic growth and address societal needs:

- Support for research and development investments that will provide the foundation for the future US bioeconomy.
- Facilitate the transition of bio-inventions from research lab to market.
- Develop and reform regulations to reduce barriers, increase the speed and predictability of regulatory processes and reduce costs.
- Update training programs.
- Identify and support opportunities for the development of public-private partnerships and precompetitive collaborations.

Specific to biochemicals and bioplastics, the Blueprint mentions increasing the availability of biobased products via funding for biomass research at United States Department of Agriculture (USDA), Department of Energy (US DOE) and Advanced Research Projects Agency-Energy (ARPA-E); transforming manufacturing through bio-innovation; and driving innovation through bio-based and sustainable product procurement by strengthening the bio-based markets program.

The USDA BioPreferred program was created by the Farm Security and Rural Investment Act of 2002 (FSRIA) and re-authorized by the Food, Conservation, and Energy Act of 2008 (frequently referred to as the 2008 Farm Bill) to increase the purchase and use of bio-based products. The USDA manages the BioPreferred program, which comprises two elements:

- Preferred procurement program for federal agencies and their contractors.
- A voluntary labeling program for the widespread consumer marketing of bio-based products.

Under the procurement program, BioPreferred designates categories of bio-based products that are required for purchase by Federal agencies and their contractors. As a part of this process, the minimum bio-based content is specified, and information on the technical, health and environmental characteristics of these products are made available on the BioPreferred website.

A bio-based product is composed wholly or significantly of biological ingredients. To be designated by the BioPreferred Program, a product must meet or exceed USDA guidelines for its product category. The bio-based content is determined via use of the American Society for Testing and Materials (ASTM) Method D6866. In addition, the BioPreferred Program has developed a voluntary labeling program for the marketing of bio-based products. Under the voluntary labeling program, bio-based products that meet the BioPreferred program requirements carry a distinctive label for easier identification by the consumer.

In the United States, at both Federal and State level, numerous programs have been set up to stimulate the construction of new plants (producing bio-based products) and/or new biorefineries. As part of the US Farm Bill, the Biorefinery Assistance Program provides grants and loan guarantees for the development, construction and retro-fitting of commercial-scale advanced biorefineries. The Biorefinery Assistance Program includes funding for grants for demonstration scale plants up to 30% of costs, and loan guarantees for commercial scale plants (up to USD 250 million per plant).

## SECTION 6. Key players in bioplastics production today and going forward.

When considering the key players in bioplastics today and in the future as the industry continues to grow, four factors must be considered:

- (a) The overall trends within the bioplastics industry in terms of single use disposables and the increasing introduction of durable bioplastics and their chemical building blocks.
- (b) The increasingly global nature of the industry.
- (c) The replacement of oil as a major energy and carbon source by Natural Gas.
- (d) The over reliance on food crops and ongoing developments in alternative feedstocks.

### **(a) The overall trends within the bioplastics industry in terms of single use disposables and the increasing introduction of durable bioplastics and their chemical building blocks.**

Compostable/biodegradable plastics form a large part of the bioplastics market. Compostable plastics will still grow in use, primarily in the single use disposable foodservice ware and agricultural film markets. The key products in this sector are PLA, starch blends, PHA's, polybutylene succinate and Ecoflex. The major players in PLA today and their projected volumes in 2020 are shown Table 18 below.

**Table 18**  
**Major PLA Players and Projected Volumes**

Company	Locations	2013 Capacity (tonnes)	2020 Projected Capacity (tonnes)
NatureWorks, LLC	USA/Thailand	150,000	450,000
Purac/Corbion	EU/Thailand	75,000*	150,000*
Zhejiang Hisun	China	5,000	20,000
Nantong Jiuding Biologic	China	5,000	5,000
Shenzhen Bright China	China	10,000	10,000
Shanghai Tong-Jie-Liang	China	3,000	10,000
Futero (Galactic/Total)	EU	1,500	5,000
Teijin	Japan	1,200	5,000
Pyramid	Germany	5,000	60,000
<b>Total Capacity</b>		<b>255,700</b>	<b>715,000</b>

\* Purac/Corbion actually sells the intermediate lactide to companies such as Synbra who then produce PLA for their own use and also sell PLA to others. However, by 2020, Corbion is also projected to be selling PLA through its relationship with Indorama in Thailand.

NatureWorks and Corbion will remain the dominant players in PLA. Geographically, the increased PLA capacity will be located in countries such as Thailand where cassava is plentiful.

There are new players also emerging such as Plaxica.<sup>104</sup>

<sup>104</sup>. <http://www.plaxica.com/>.

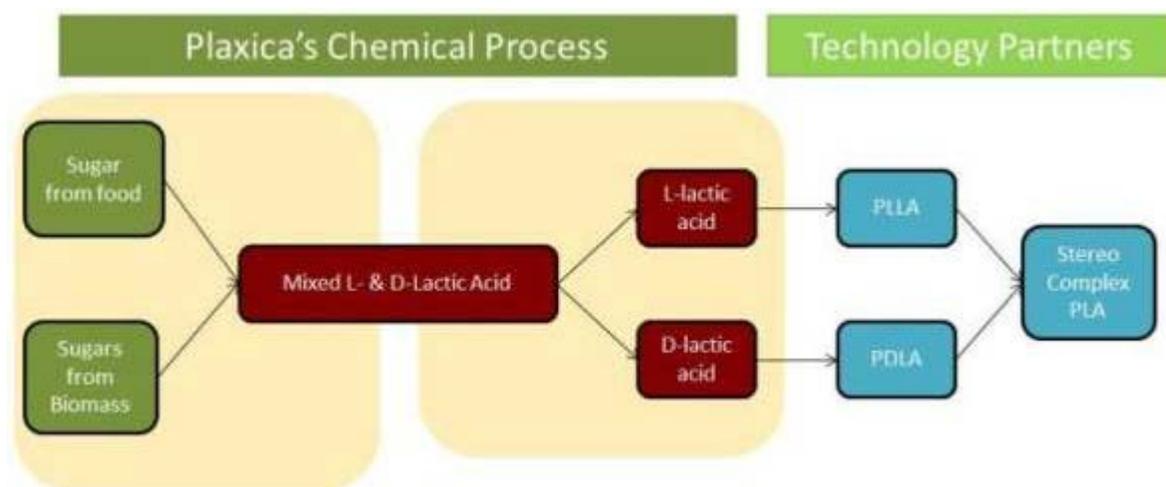
Plaxica uses a chemical process to convert a wide variety of sugars to lactic acid and lactide which can then be polymerized to produce PLA. Their process produces both the L and D enantiomers of lactic acid / lactide. The ratio of L and D can be controlled to suit the polymer application. The process can apparently be modified to reclaim the waste material from PLA production and use, including post-consumer PLA, and chemically converting it into D or L lactic acid. A schematic of Plaxica's process<sup>105</sup> is shown in Figure 31.

<sup>105</sup>. <http://www.plaxica.com/wp-content/uploads/2013/06/Plaxica-Full-Process-for-Website.jpg>

Plaxica is following a technology licensing strategy but, given the developed nature of the existing routes to PLA, it is not clear as to how successful they will be.

Another very recent development<sup>106</sup> is the announcement by Catalysta on June 14, 2014 that it has produced lactic acid from methane at lab scale. Catalysta is working under research collaboration with NatureWorks LLC.

<sup>106</sup>. <http://www.bioplasticsmagazine.com/en/news/meldungen/Calysta.php>



**Figure 31. Schematic of Plaxica's Process for PLA.** Figure modified from<sup>103</sup>.

The joint development program was started in June 2013 between Catalysta and NatureWorks and is focused on creation of a commercially viable methane-to-lactic-acid process. The key aims are providing a structurally simplified, lower cost Ingeo production platform and diversifying NatureWorks' feedstock portfolio.

For the starch blends the two major players are Novamont in Italy and Biotec in Germany. Novamont has the dominant patent portfolio and its recent JV with Genomatica to produce butane 1,4 diol places it in an excellent position to continue to improve its portfolio of products. Also the recent banning of non compostable bags in Italy almost guarantees that Novamont will be the dominant producer for the compounded starch products.

The Polyhydroxy alkananoate field is much more difficult to predict. The key players today are shown in Table 19.

**Table 19. Key PHA Players**

Country	Company	Product	Capacity
USA	Metabolix	P-3HB-4HB	Sourcing from China
	Meredian	PHBH	Claim 30,000 tons in 2014
Brazil	PHB Industrial S/A	P-3HB	About 50 tons/y
Japan	Mitsubishi GAS Chemicals	P-3HB	About 10 tons/y
Germany	Biomer	P-3HB	Small scale
Italy	Bio-on	PHBH	Claim 10,000 tons
Canada	BioMatera Inc.	P-3HB	Capacity unknown
China	Tianjin Green Bioscience/DSM	P-3HB-4HB	Claim 10,000 tons
	Ecomann	P-3HB-4HB	Claim 4,000 tons
	Tianan Biologic	P-3HB-3HV	Presently 2,000 tons

Metabolix was considered the “front runner” in the PHA field until the dissolution of its relationship with ADM in 2012. Presently, they are sourcing PHA from Tianjin Green Bioscience in China. The relationship with Antibióticos in Spain, who were going to produce PHA’s on behalf of Metabolix, also does not seem to be proceeding. More recently, Meredian in Bainbridge, Georgia, has announced it is bringing on up to 27,000 tonnes of PHA capacity in the later part of 2014. Meredian acquired their PHA technology from P&G in 2007 that originally acquired it from Kaneka and marketed under the trade name Nodax™. P&G had planned a commercial scale up in 2006 with Kaneka Corp. of Osaka, Japan, which still holds intellectual property for the technology. It is not clear why P&G decided to sell Nodax. Meredian claims it uses plant-based fatty acids to create PHA through fermentation using genetically engineered organisms.

Today, the dominant PHA producer appears to be Tianjin Green Bioscience. In 2009, The DSM Venture Capital, a unit of Dutch DSM Group, invested 20 million U.S. dollars in Tianjin Green Bioscience. Their claimed capacity is 10,000 tonnes.

A major concern of PHA’s is their present economics. Metabolix has tried to develop the market selling their PHA at around \$2.50/lb. This is much too expensive for these polymers to compete against conventional plastics. Meredian has claimed it can produce and sell their PHA for around \$1.00/lb but this has yet to be demonstrated. Recently new entrants into the PHA field are claiming they can use carbon dioxide and/or methane gas to produce PHA’s with very favorable economics.

Three companies appear to be developing processes based on this pathway:

- Mango Materials<sup>107</sup>  
<sup>107.</sup> <http://www.mangomaterials.com/>
- Oak Bio<sup>108</sup>  
<sup>108.</sup> <http://www.oakbio.com/>.

- Newlight Technologies<sup>109</sup>  
<sup>109</sup>. <http://www.newlight.com/>.

It is too early to tell if this approach will enable PHA's to become more commercially viable.

Polybutylene succinate (PBS) has been of interest as a bioplastic for some time but its growth has been restricted due to its high cost. The earliest producer was Showa High Polymers (now Showa Denko) that still produces this material under the trade name of Bionolle™. They have approximately 6000 tonnes capacity. There are also other smaller producers in Korea such as SK Chemicals and Samsung Fine Chemicals. Polybutylene succinate from these suppliers is produced completely from petro chemicals. With the accelerating developments in the production of biobased succinic acid and butane diol the potential is emerging to produce PBS purely from renewable resources.

Present players for bio succinic acid include: BioAmber, Myriant, Reverdia (a joint venture between Dutch chemical company DSM and France-based starch derivatives producer Roquette), and Succinity (BASF and Corbion JV).

The intense activity around succinic acid highlights a renewed trend in bioplastics where large global petrochemical companies are partnering with agricultural companies or smaller technology developers to either re position themselves in the marketplace or replace their existing petro based products with renewable equivalents. One specific example in regard to succinic acid and other bio materials is DSM. In 2001 DSM established a new Division called DSM Venturing which operates independently of their mainstream polymer activities. This arm of DSM, has invested in more than fifty emerging innovative companies in the US, Europe and Israel. Besides succinic acid, DSM venturing has invested in Tianjin Green Bioscience, Novomer, Segetis and Verdezyne.

BASF has partnered with Corbion to produce succinic acid. In addition it presently produces Ecoflex, which is a fully synthetic biodegradable polyester. To protect its investment in conventional polymers such as PBT and also to enable the conversion of Ecoflex to a renewable biobased product, BASF has also invested in Genomatica and plans to produce Bio butane 1,4 Diol using their process. BASF has also teamed up with Renmatix to scale up the Renmatix Plantrose™ process for the production of industrial sugars based on lignocellulosic biomass. Finally BASF has a relationship with Amyris who acquired Draths and their technology to potentially produce bio terephthalic acid.

In addition to DSM and BASF we also see DuPont Industrial Biosciences division not only marketing PTT but also teaming up with The Goodyear Tire and Rubber Company to produce isoprene from renewable resources under the Biolsoprene™ trade mark.

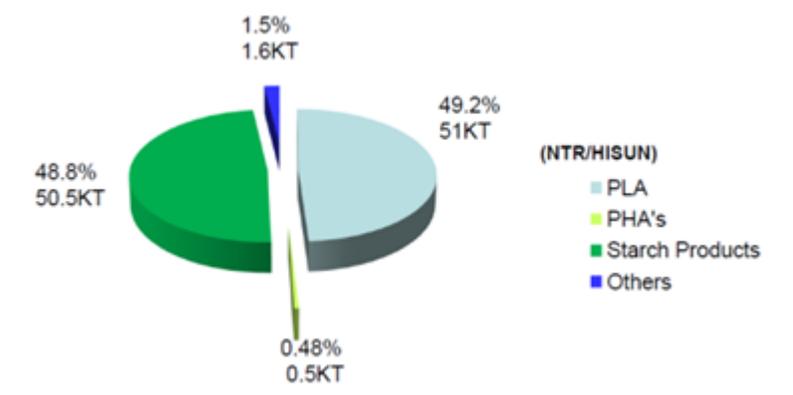
Another large European Company Lanxess, a leading specialty chemicals company, has recently invested in BioAmber to manufacture bio succinic acid at the Lanxess site in Sarnia Ontario and also jointly develop phthalate-free plasticizers based on succinic acid.

Earlier in 2011, Lanxess teamed with Braskem to develop a bio ethylene propylene diene monomer (EPDM). EPDM rubber is the third most-used synthetic rubber after styrene-butadiene rubber (SBR) and butadiene rubber. In 2013 Lanxess and Genomatica announced that Lanxess had run a production campaign of bio-based PBT in Lanxess' world-scale production plant using 20 tonnes of bio-based BDO made with Genomatica's commercially-proven process. This BDO fully complied with the demanding Lanxess specifications for petro-based BDO allowing a direct feed of 100 percent bio-based BDO into the continuous production process. The properties and the quality of the resulting bio-based PBT are fully equivalent to conventional petro-based PBT with regard to all tested parameters. The world-scale PBT plant, with a capacity of 73,000 tonnes per year, is located in Hamm-Uentrop, Germany and operated as a joint venture in which Lanxess has a share of 50 percent. In addition to these ventures in 2011 Lanxess announced a relationship with Gevo to purchase its biobutanol to produce bio butyl rubber.

These are just a few examples of how large petrochemical based companies are beginning to enter the bio space. It is believed that, as the bio industry develops outside of the early generation PLA and starched-based products, we will see many more large petrochemical-based companies move into the bio space either as partners or by acquisition of the smaller companies presently involved in the production of chemical building blocks from renewable resources. Over the coming years, non-biodegradable plastics based on renewable feedstocks will become increasingly important players in the bioplastics market. Players and developments in this area have already been covered extensively in Section 3 (pages 19-71) of this report.

**(b) The increasingly global nature of the industry.**

Bioplastics entered the marketplace primarily in the USA and Europe and the market was essentially dominated by PLA and compounded starch products. In 2009 Jim Lunt & Associates estimated the breakdown of bioplastics sales globally to be almost equally divided between PLA and starch blends with minor amounts of durable plastics being produced. This breakdown is shown in Figure 32.



**Figure 32. 2009 Breakdown of Bioplastics.**

PLA was produced primarily by NatureWorks in the USA and the starch products primarily by Novamont and Biotec in Europe. By 2011, as the market developed and the diversity of products and manufacturing volumes increased so has the number of players and manufacturing locations. Bio PE is produced from sugar cane in Brazil, bio ethylene glycol is manufactured in India from bioethanol produced in Brazil, and Purac has moved its lactide operations to

Thailand. As the bio-plastics industry further develops, Thailand in Asia is projected to become a significant source of cassava feedstock. Sugar cane in Brazil will also remain as a significant source as will castor oil in India and palm oil in Malaysia.

According to European Bioplastics<sup>110</sup>, both Europe and the USA will decline as major suppliers of feedstocks but will still be dominant users of bioplastics and bio building blocks for the foreseeable future- see Figure 33.

<sup>110</sup> <http://en.european-bioplastics.org/multimedia/>

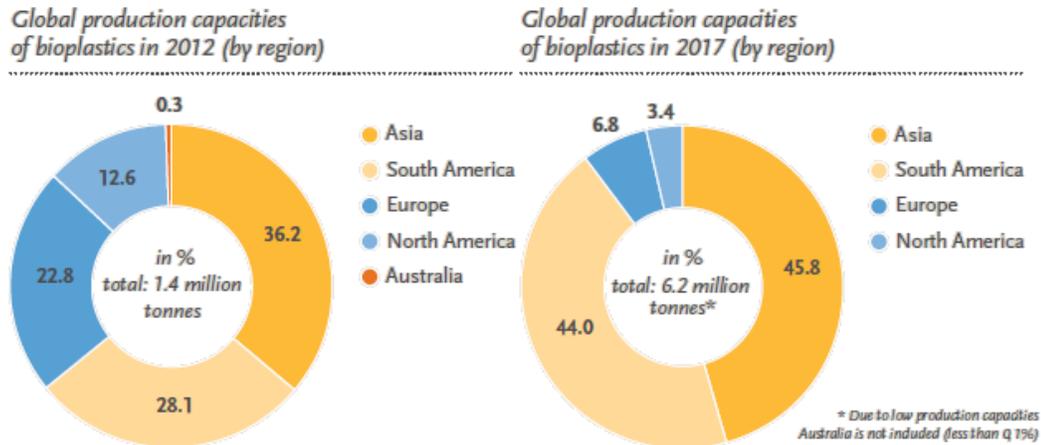


Figure 33. Global Trends in Bioplastics Capacities. Figure modified from<sup>106</sup>.

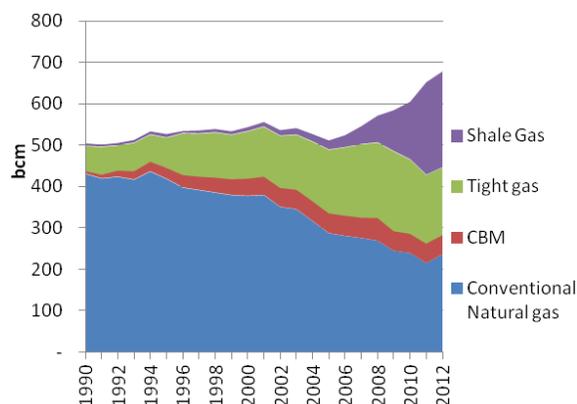
**(c) The replacement of oil as a major energy and carbon source by shale gas.**

The shale gas revolution has led to strong falls in energy prices, reducing significantly the raw material costs of the US petrochemical industry.<sup>111</sup> Between 2008 and 2012, US gas prices fell by two thirds. Ethane comes from natural gas liquids (NGLs) contained in shale gas, and used by the US petrochemical industry as the raw material to make ethylene. Its price fell by 55% between 2008 and 2012. These price cuts are giving the US petrochemical industry a significant competitive advantage, and profits are exploding. The United States has become the region in the world with the second lowest energy and raw material prices, just after the Middle East.

<sup>111</sup>. <http://www.ifri.org/downloads/versionengscg29nov.pdf>

Hydraulic fracturing has allowed the United States to tap non-conventional gas and oil resources, modifying the US energy scene radically. Just as gas production in the United States was falling, it then experienced a 24% rise between 2007 and 2012. This rise has been due to the production of shale gas, which today accounts for 34% of US gas output. In 2012, shale gas output rose to 230 billion cubic meters - more than five times its 2007 level.<sup>112</sup> This trend is shown in Figure 34.

<sup>112</sup>. <http://www.eia.gov/naturalgas/>



**Figure 34. US Gas Production 1990-2012.**

Figure modified from<sup>112</sup>.

The explosion in shale gas and the significant reduction in the price of ethane have led to a reconsideration of the production of olefinic polymers such as polyethylene and polypropylene from renewable resources. Braskem has delayed its planned new capacity in bio PE and Bio PP and Dow has also cancelled its plans with Mitsui for a bio PE plant in Brazil.

The shale revolution in North America has also had a major impact on petrochemical production in Europe. Low cost feedstocks associated with shale gas have altered the production landscape, as steam cracker operators capitalize on the advantage yielded by cheap natural gas liquids, particularly ethane. Chemical majors such as Dow, ExxonMobil Chemical, Formosa Plastics Corporation USA, Sasol, Chevron Phillips Chemical and Shell are among those that have announced new steam cracker capacities. Brownfield projects encompassing expansions, debottlenecks and restarts are planned by LyondelBasell, Ineos, BASF, Westlake and Dow. In combination, these projects could increase North American ethylene capacity by more than 11 million tonnes/year by 2017.

Meanwhile, many producers with the flexibility to adjust feedslates at the cracker level have already increased ethane input. The ongoing shift to lighter feedslates has, however, had a significantly negative impact on heavier co-products such as propylene, butadiene and aromatics, with yields cut by as much as 55%. The North American aromatics market has been particularly impacted, with benzene, toluene, and xylenes (BTX) production declining in recent years.<sup>113</sup>

<sup>113</sup>. <http://www.platts.com/IM.Platts.Content/InsightAnalysis/IndustrySolutionPapers/aromatics-shale-revolution.pdf>

How these trends will ultimately affect the growth in bioplastics is not completely clear. Aromatics are difficult to produce from sugar sources but companies such as Virent, Gevo and Anellotech are already working on the production of para-Xylene. Other recent entrants include M&G who has strategic relationships with Chemtex, Genomatica and Amyris. M&G has potential to produce bio TPA using the t,t muconic acid route developed by Draths (acquired by Amyris) and Genomatica. Other possible players include Primus Green Energy, U. Mass Amherst, and Micromidas who also claim possible routes to para Xylene.

Avantium is also working on the production of furan dicarboxylic acid (FDCA) as a replacement for terephthalic acid in aromatic polyesters.

**(d) The over reliance on food crops and developments in alternative feedstocks.**

Food crops such as corn, sugar beet, cassava are the major feedstocks for the bioplastics industry. However, with the advent of biofuels such as biodiesel and bio ethanol, consumer concern has arisen about the impact of these non food uses on the price and availability of the food supply. Although use for bioplastics is extremely small (less than 0.5% of the US corn market), inevitably this concern has spilled over to the bioplastics market. Possibly, the single most dominant development for bioplastics in the next few years will be the shift from food crop starch and sugars to second generation nonfood alternatives. Consumers have made it very clear that biopolymer production should not compete with the world's food supply.

**Availability of Second Generation Feedstocks.**

By far the largest group of potential secondary feedstocks for conversion to sugars is ligno cellulosics. Common ligno cellulosics include:

- **Woody Biomass**
  - Forest residues
  - Wood waste
  
- **Non-Woody Biomass**
  - Agricultural residues:
    - Straws (wheat, barley, rice)
    - Bagasse (sugarcane, sweet sorghum)
    - Stover (corn, milo)
    - Algae
  
- **Organic Waste**
  - Animal waste
  - Sewage sludge.

Today, demand for such feedstocks is driven primarily by the search for alternative energy sources to petroleum. The bioplastics industry is a very small proportion (less than 1% of all plastics). The global plastics industry is estimated at around 230 million tonnes but is projected to experience significant growth over the next 5-10 years. To produce bioplastics from these feedstocks we are primarily looking at conversion to sugars which can then be further utilized to produce the basic building blocks for bioplastics. For bioplastics use we do not need a large proportion of the global biomass availability. However, sugars for bioplastics will probably compete with sugars for fuel or be a more value added side stream from a biorefinery or co-located biomass to sugar producing facility.

**Biomass Supply Costs**

Costs for biomass supply to a biofuel or sugar conversion facility, strongly depends on regionally specific conditions such as biomass potentials related to the total area of the region, infrastructure as regards the transportation network and its availability, and of multi faceted plants that have access to roads, rail and /or harbors. Since as yet, there are no established markets for most of the primary agricultural residues, the data on costs are not precise. Price estimates for second generation feedstocks and their availability vary significantly between

emerging and developing countries. For example, pricing for sugar cane tops and leaves range from \$0.003 to \$0.008/kg in Brazil, \$0.008-0.015/kg in Thailand and \$0.02-0.03/kg in India.<sup>114</sup>

<sup>114</sup> [http://www.iea.org/publications/freepublications/publication/biofuels\\_exec\\_summary.pdf](http://www.iea.org/publications/freepublications/publication/biofuels_exec_summary.pdf)

In addition, biomass supply costs increase for larger scale biofuels plants due to higher biomass demand (around 540,000tonnes/yr for a large commercial plant). The increased cost is due to increasing transport distances and more complex logistics such as higher handling and storage costs. For agricultural and /or forestry residues, such as straw or logging chips, their lower bulk density further increase the costs. Moisture content of biomass also influences cost.

Typical costs for forest and agricultural residues in the USA in 2009<sup>115</sup> are given in Table 20.

<sup>115</sup> [http://www.epa.gov/chp/documents/wbnr062509\\_hedman.pdf](http://www.epa.gov/chp/documents/wbnr062509_hedman.pdf).

**Table 20. Typical USA biomass costs in 2009.** Figure modified from<sup>115</sup>.

Resource	Energy Content, Wet (Btu/lb)	Energy Content, Dry (Btu/lb)	Cost (\$/ton)	Cost (\$/MMBtu)
Forest residue	5,140	8,570	15 - 30	1.50 - 2.95
Forest thinnings	5,140	8,570	15 - 30	1.50 - 2.95
Mill residue		8,570	8 - 50	0.50 - 2.95
Corn stover	5,290	7,560	20 - 40	1.90 - 3.80
Wheat straw	5,470	6,840	40 - 50	4.00 - 5.00
Hybrid poplar/willow	4,100	8,200	30 - 60	4.75 - 7.50
Switchgrass	6,060	8,670	35 - 50	2.90 - 4.25
Urban wood waste	4,600	6,150	3 - 24	0.50 - 2.80
Food processing residue	Case by case			1.25 - 2.50
Landfill gas	350 - 650 Btu/scf			1.00 - 3.00*
Manure biogas	600 - 800 Btu/scf			Variable*
WWT biogas	500-650 Btu/scf			Variable*

\* May require treatment and clean-up costs

By comparison, corn price in the USA is presently \$4.50/bushel. (\$0.18/kg)

Corn dextrose sugar price cost in the USA in 2013 was 40-44¢/kg.

### Biomass Conversion Technologies

Unlike first generation feedstocks such as corn or sugar beet, second generation ligno cellulosic feedstocks are much more recalcitrant materials that require intensive labor and high capital costs for processing. In addition the chemical composition of the feedstock varies depending on type- Figure 35.<sup>116</sup>

<sup>116</sup> <http://www.katzen.com/ethanol101/Lignocellulosic%20Biomass.pdf>

Lignocellulosic materials	Cellulose	Hemicellulose (%)	Lignin (%)
Hardwood stems	40-55	24-40	18-25
Softwood stems	45-50	25-35	25-35
Nut shells	25-30	25-30	30-40
Corn cobs	45	35	15
Grasses	25-40	35-50	10-30
Paper	85-99	0	0-15
Wheat straw	30	50	15
Sorted refuse	60	20	20
Leaves	15-20	80-85	0
Cotton seed hairs	80-95	5-20	0
Newspaper	40-55	25-40	18-30
Waste papers from chemical pulps	60-70	10-20	5-10
Primary wastewater solids	8-15	NA	24-29
Swine waste	6.0	28	NA
Solid cattle manure	1.6-4.7	1.4-3.3	2.7-5.7
Coastal Bermuda grass	25	35.7	6.4
Switchgrass	45	31.4	12.0

**Figure 35. Composition of Various Lignocellulosic Feedstocks.** Figure modified from<sup>116</sup>.

**Cellulose** is a very large polymer molecule composed of many hundreds or thousands of glucose molecules (polysaccharide). The molecular linkages in cellulose form linear chains that are rigid, highly stable, and resistant to chemical attack.

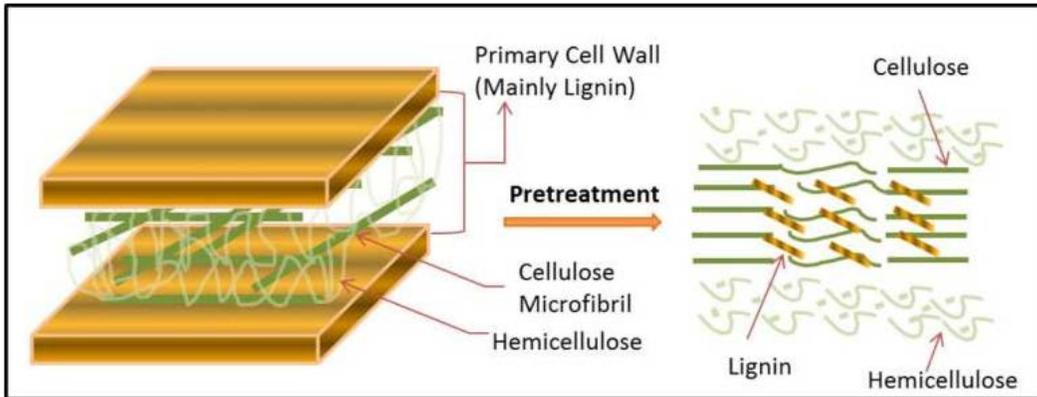
**Hemicellulose** consists of short, highly branched, chains of sugars. It contains five-carbon sugars (usually D-xylose and L-arabinose) and six-carbon sugars (D-galactose, D-glucose and D-mannose) and uronic acid. Hemicellulose is amorphous and relatively easy to hydrolyze to its constituent sugars. When hydrolyzed, the hemicellulose from hardwoods releases products high in xylose (a five-carbon sugar). The hemicellulose contained in softwoods, by contrast, yields more six-carbon sugars.

There is more experience fermenting six-carbon sugars than the five-carbon sugars, but both are valuable fermentation feedstocks, especially with recent advances in fermenting five-carbon sugars.

**Lignin** is a polymer constructed of non-carbohydrate units that are not fermented, but must be separated from the cellulose and hemicellulose by chemical and other means.

Conversion of lignocellulosic biomass to fermentable sugars represents significant technical and economic challenges both in the development of effective pretreatments as well as highly efficient and cost-effective processes for conversion of pretreated lignocellulosic substrates to fermentable sugars<sup>117</sup>. Typical technologies being developed for the key steps are shown in Figure 36.

<sup>117</sup>. <http://edis.ifas.ufl.edu/ae495>



**Figure 36. Typical Technologies for Deconstruction of Biomass.** Steps include: Destroy lignin shell protecting cellulose and hemicellulose; Increase Porosity; Reduce cellulose crystallinity; Separate out hemicellulose; Hydrolyze amorphous hemicellulose to sugars. Picture Credit-Zhaohui Tong Figure modified from<sup>117</sup>.

### Pretreatment Technologies

Since each feedstock type has a different composition and quantity of lignin then the specific pretreatment may be different. Pretreatments must improve the digestibility of lignocellulosic biomaterials, and each pretreatment has its own effect on the cellulose, hemicellulose and lignin fractions.

Mechanical pretreatment such as chipping grinding or milling is followed by various chemical techniques covering a wide range of technologies. Techniques which have been studied include steam explosion, hot water under high pressure, weak or strong acid hydrolysis, alkaline hydrolysis, ammonia fiber explosion, organo solv (methanol, butanol, ethanol acetone or ethylene glycol), hydrogen peroxide, ozonolysis, ionic liquids and biological pretreatment using microorganisms and fungi.

Of these techniques only a small number are considered to be cost effective, such as steam explosion, dilute and strong acid hydrolysis, organosolv and liquid hot water hydrolysis.

Once pretreatment has disrupted the cell wall to expose the components, removed the low molecular weight hemicellulose fraction and converted this to soluble sugars, the cellulosic portion must be converted to sugar(s) and the lignin removed.

Potential emerging leaders in the ligno cellulosic deconstruction field include:

**Tier 1:** *(Already in pilot scale, differentiated technology, closest to commercialization.)*

- Renmatix
- Virdia
- Chemtex/M&G- Beta Renewables
- American Science and Technology (AST)

**Tier 2:** *(Still in early development or focused more on ethanol use of sugars.)*

- CIMV
- Sweetwater Energy
- Weyland

**Tier 3:** *(Not clear as to uniqueness of technology, over 5 years away from possible commercialization.)*

- Blue Fire Renewables
- Comet Biorefining
- Pure Vision
- Proterro

Tier 1 players and their technologies are discussed below:

**Renmatix:**

Renmatix has developed a supercritical water extraction process for lignocellulosics.

The water-based Plantrose™ process consists of two core steps.<sup>118</sup>

<sup>118</sup>. <http://renmatix.com/technology/our-technology/>

The first step is fractionation of biomass to remove oligomeric hemi cellulose sugars followed by separation of the remaining solids which contain cellulose and lignin. The second is cellulose hydrolysis of the pretreated solids under elevated conditions utilizing supercritical water, or water at higher temperatures and pressures, as the primary solvent. The relative ease of hydrolysis of the hemicelluloses compared to the recalcitrant cellulose necessitates this two-step process in order to preserve the C5 sugar that would be rapidly destroyed under the more severe conditions necessary for cellulose dissolution into C6 sugar.

As part of step one, the biomass first undergoes size reduction, as necessary, and is then conveyed to a storage silo. The stored solids are slurried with water and pumped and heated to reaction temperature and then fed to the fractionation reactor where the reaction takes place. The products from the fractionation reactor are then sent to solid/liquid filtration and stored.

The solids from the fractionation process consist predominantly of cellulose and lignin. These solids are sent to a blend tank where they are re-slurried by mixing with water and then pumped into the system at pressure and preheated. The preheated slurry is further treated with hot compressed water and undergoes a rapid reaction. The products from this reaction are then cooled and filtered. Remaining solids, in the form of clean, odorless lignin, are collected.

Where necessary, the separate C5 and C6 soluble oligomer streams are easily and quickly transformed to monomers through a catalytic process. The company claims it can produce sugars at the same cost as pure sugars from food crops such as sugar cane, sugar beet or corn.

The technology was originally developed using hard wood biomass and Renmatix has a 2.7 dry tonnes/day unit in Kennesaw, Georgia. This has been operating since 2011. In January of 2013, Renmatix commissioned a smaller plant in Pennsylvania. According to Fred Moesler, CTO of Renmatix, the pilot unit in Georgia, is focused on the commercial development of woody biomass. The unit in Pennsylvania is the next evolution in the process by expanding the types of

feedstocks that can be processed, thereby demonstrating the flexibility of the process. Supposedly this second pilot unit will examine the capability to use a variety of feedstocks such as perennial grasses, agricultural residues, softwoods, and municipal solid waste streams. According to Moesler, the key to Renmatix's business success relies on utilizing a variety of feedstocks.

In 2013, Renmatix announced agreements with BASF, Virent and Finland based UPM.

**Viridia:**

A schematic of the Viridia process is shown in Figure 37.<sup>119</sup>

<sup>119</sup><http://www.lsuagcenter.com/MCMS/RelatedFiles/%7B36CA0490-FF2B-4DBC-967F-0CAA8D210CCD%7D/15.Baniel.pdf>.

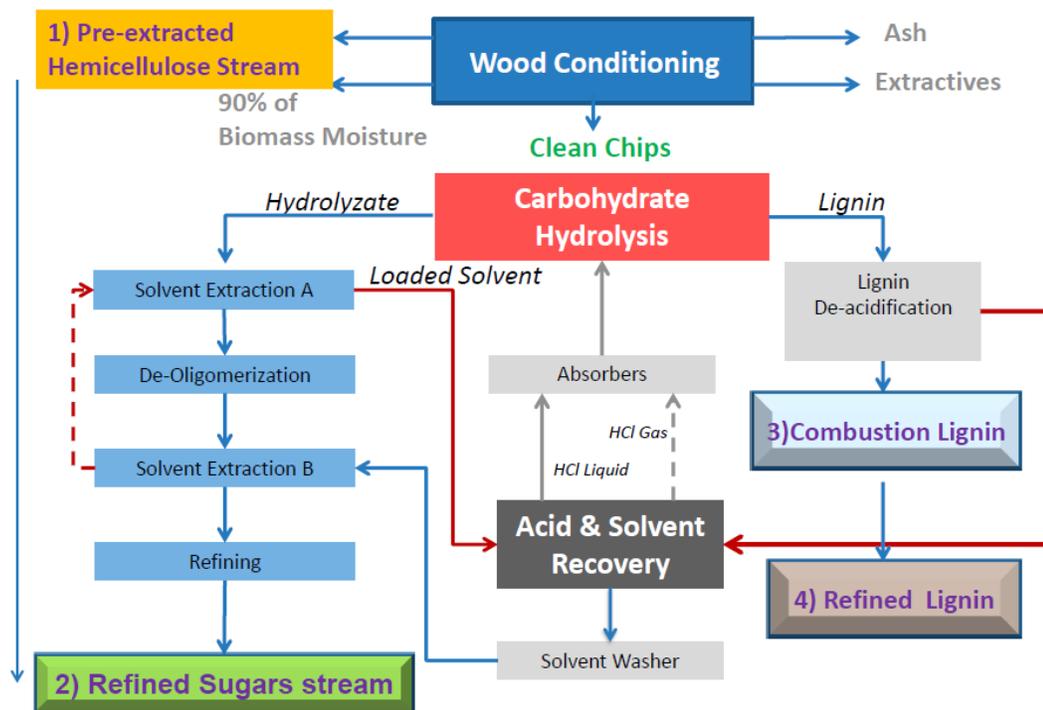


Figure 37. Viridia Case™ Process for Lignocellulosic Extraction. Figure modified from<sup>117</sup>.

Viridia, founded in 2007, was formerly known as HCL Cleantech. Its process is trademarked as CASE™. The basic technology was used extensively during World War II to produce C6 sugars. The use of fuming acid (HCL gas) in what is known as the Bergius process ensured high yields, but the costs of recovery and reconcentration of the hydrochloric acid made the original process costs too high for economic viability.

Viridia claims to have improved the recovery of the hydrochloric acid and dramatically improved the economics of the original technology while preserving the high yields and sugar purity of the original process.<sup>120</sup>

<sup>120</sup><http://www.virdia.com/>

The specific improvements are believed to include lower temperature extraction and the use of a solvent (acetone) to recover the hydrochloric acid. Viridia claims its sugars contain no inhibitors and ferment well when compared to corn or cane sugars. The sugars have negligible degradation products such as furfurals, HMF, acetic acid and soluble phenolic compounds.

Viridia also claims it can use several biomass feedstocks, but today is focused on the use of loblolly pine as the primary starting material. Its process involves a pretreatment that removes the extractives and ash present in all biomass. The presence of the extractives during concentrated acid hydrolysis can complicate the process, reduce productivity and may contaminate the final product. The remaining material is hydrolyzed using cold concentrated hydrochloric acid to generate soluble C5 and C6 sugars. The sugar hydrolyzate and lignin exit the process as separate streams, and are de-acidified and refined. The hydrolyzate yields a stream of concentrated fermentable monomeric C5 and C6 sugars that can be used in a large number of food and feed fermentation applications, as well as renewable fuel and chemical applications. The resultant dry, low chlorides, low ash lignin solids are said to have a significant energy value and commercial value in applications such as graphite fibers.

In April 2012, Viridia announced a deal with the Mississippi Development Authority to build a plant to derive sugar from wood chips, a plentiful byproduct of the State's forestry industry. Viridia is presently operating a 0.0114 tonnes/day pilot/demonstration unit in Danville, VA. The company has not disclosed when it will commence large scale plant construction, but in early 2012 announced plans for its first commercial plant in Mississippi. This plant was projected to be on line by 2014 and would process 340,000 tonnes of wood a year into 136,000 tonnes of sugar.

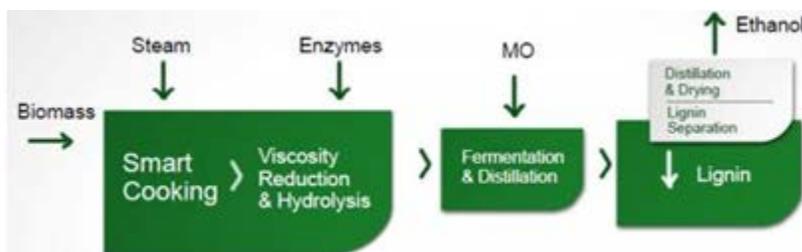
#### **Technology/Business Risks and Time to Market**

From a technology perspective, the process is proven. It is uncertain as to whether they can use feedstocks other than loblolly pine or eucalyptus. The company has stated that their acid extraction process is not competitive with enzyme technologies if used for agricultural waste. Business wise, a plant in 2014 appears unlikely at this point. There have been concerns expressed around the use of hydrochloric acid from an environmental perspective. Viridia has not been successful in attracting non VC partners although it does have a relationship with Virent, a potential user of its sugar. It has also received \$75 million from the Mississippi Development Authority to build manufacturing plants in the state.

## **Beta Renewables:**

A schematic of the Beta Renewables Proesa® Process is shown in Figure 38.<sup>121</sup>

<sup>121</sup>. [http://www.bio.org/sites/default/files/beta%20renewables%20proesa%20technology%20june%202013\\_bio\\_michele\\_rubino.pdf](http://www.bio.org/sites/default/files/beta%20renewables%20proesa%20technology%20june%202013_bio_michele_rubino.pdf)



**Figure 38. Beta Renewables lignocellulosic extraction process.**

The Proesa process technology benefits include; feedstock flexibility, fully integrated with continuous equipment to enable large scale plants, continuous process for optimal sugar extraction and low enzyme dosage, and best in class technology with lowest capex and opex backed with performance guarantees. Figure modified from<sup>121</sup>.

Beta Renewables is a \$350 million (€250M) joint venture formed from the Chemtex Engineering Division of Gruppo Mossi & Ghisolfi (M&G) along with capital investment firm TPG. Recently, Novozymes also acquired a 10% share in Beta Renewables for \$ 115 million (€ 90 million).<sup>122</sup>

<sup>122</sup>. <http://www.betarenewables.com/>

Beta Renewables has licensed the Proesa™ process from M&G and has the exclusive right to license the technology worldwide. The process includes a steam pretreatment step followed by enzyme hydrolysis to produce C5 and C6 sugars. The enzyme hydrolysis is claimed to be much faster than competitive technologies and said to be covered by 21 pending patents. Preferred feedstocks are said to include giant reed, miscanthus or switch grass and agricultural waste (such as sugarcane bagasse and straws).

Beta Renewables has run a demonstration-scale biomass plant continuously since mid-2009, with dedicated areas for partners that integrate PROESA™ with its downstream conversions. Beta Renewables has also developed a supply chain that extends into the local agricultural community around Crescentino. Beta has also built the world's first commercial scale cellulosic ethanol plant in Crescentino, Italy. This plant began production at the end of 2012, with a design capacity of 60,000 tonnes/yr ramping up from an initial 40,000 tonnes. Feedstocks are non-food biomass (Arundo donax and wheat straw). A similar project is under development in North Carolina.

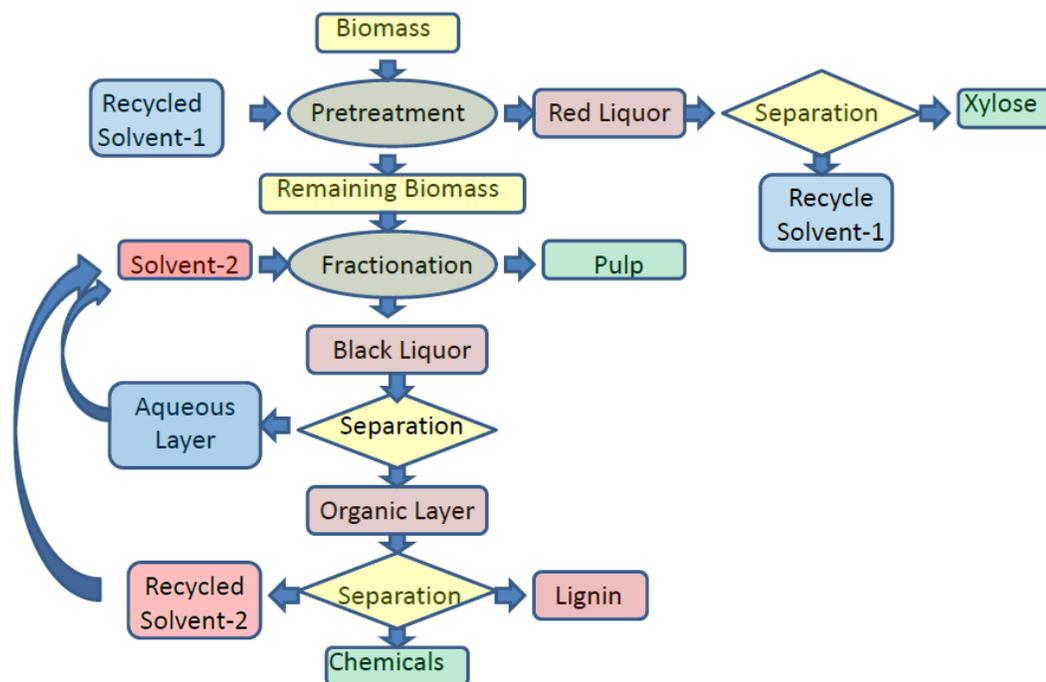
### **Technology/Business Risks**

The Beta Renewables technology appears to be robust and has been demonstrated at large scale. One key concern is how much sugar will actually be available for use by other companies that are not looking to produce bioethanol.

**American Science and Technology (AST):**

A schematic of AST's process is shown in Figure 39. AST has collaborated with the University of Wisconsin - Stevens Point (UWSP) to develop an Organosolv process for the fractionation of whole biomass and converting its components to valuable fuels and chemicals.<sup>123</sup>

<sup>123</sup>. <http://www.amsnt.com/>



**Figure 39. American Science and Technology Extraction Process.** Figure modified from<sup>123</sup>.

In the Organosolv process, all three different components of the biomass (hemi, cellulose, and lignin) are separated in a single step. Currently, AST have two reactors (0.5-2 Kg biomass) at UWSP to screen and optimize the process. AST also has a pilot plant which can process 40-80 kg of whole biomass in 1.5-2 hours. Once the components are separated a 100L hydrolysis unit (ceramic) is used to convert the oligomers to monomer sugars. The lignin is used in two pyrolysis units to produce bio-oil and hydrocarbon fuels through a catalytic process.

In 2013, American Science and Technology (AST) announced the launch of a new subsidiary, BioRen Chemical. Serving as AST's manufacturing division, BioRen is currently in the process of setting up a concentrated sugar production line, expanding on the current biorefinery plant established by AST in Wausau, WI.

BioRen is working closely with a Fortune 500 client to convert its lignocellulosic biomass to concentrated sugar. Initial output will be approximately 5 tonnes/year, however, plans are in place to scale up production to 25 tonnes/year by the end of 2014, and up to 1000 tonnes/year by the end of 2015. Bioren's parent company, American Science and Technology has developed

a proprietary process to produce concentrated sugar syrup from non-food, lignocellulosic biomass feedstock. This process reduces the production cost of sugar syrup, reduces the use of external energy, and reduces the amount of water and expensive distillation setup. The sugar serves as a key building block for the production of many products including biofuel, biochemicals, and bioplastics.

Through collaboration with the University of Wisconsin - Stevens Point (UWSP), a patented Organosolv process was developed for the fractionation of whole biomass and converting its components to valuable fuels and chemicals. In this process, all three different components of the biomass (hemi, cellulose, and lignin) are separated in a single step, increasing efficiency and profitability.

Little is known about the economics of AST's process. Commercially the Organosolv process has been used in industrial paper-making processes and has been considered in the context of both pulp and paper manufacture and biorefining for subsequent conversion of cellulose to fuel ethanol.

## **SECTION 7. Summary and recommendations for how AURI could contribute and participate in driving the growth of the bioplastics industry.**

To assist AURI to evaluate opportunities that may exist for it to participate in the growing bioplastics industry a comprehensive review of the various facets of the industry has been carried out.

The bioplastics industry is growing at an overall estimated 19% CAGR and this is expected to continue into 2020. Compostable single-use plastics are maturing with very few potential new significant entrants other than polybutylene succinate (PBS) and possibly ketals in the near future. Growth in these materials will be more geographic in nature as opposed to capturing new market segments. There will be some limited penetration of more durable intermediate to longer life applications but this will not be significant. The key players will remain essentially unchanged for the foreseeable future.

Two other bioplastics developments show significant growth potential:

- (1) The development of completely or partial biobased analogues of conventional plastics has accelerated since the performance spectrum and markets are well known and a large part of the manufacturing infrastructure is already in place. Existing chemical building blocks and resultant polymers are being developed from renewable resources. There are also new polymers such as polyethylene furanoate being developed which show promise since they can, to a large extent, also use existing capital infrastructure. Recent developments in cheap and plentiful supply for shale gas are creating questions around the future competitiveness of bio based polyolefin initiatives and even bio ethylene glycol for use in PET. Perhaps, unexpectedly, this dynamic may actually accelerate developments around bio-based aromatics such as terephthalic acid, benzene, toluene and xylenes since these molecules are not available in shale gas as opposed to naphtha.
- (2) A second and potentially more significant major trend for the future of bioplastics is the drive to move from food-based starch and sugars to alternative non-food feedstocks. One of the prime classes of second generation feedstocks being investigated is agricultural waste such as corn stover, wheat straw and energy grasses. The present players do not have the ready access to these types of biomass and often are under pressure to demonstrate their technology using one specific feedstock.

### **Specific Recommendations for AURI to participate in bioplastics:**

- (a) Potential opportunities for AURI lie in the alternative feedstocks area. Specifically, AURI could act as a conduit to the feedstocks and also potentially become involved in the extraction technology of sugars from these materials. Companies such as AST already work with the University of Wisconsin. AURI could work with the University of Minnesota and companies such as Renmatix, Virdia and possibly AST to screen agricultural biomass and technologies for efficiency, economics, overall sustainability and ultimate commercial viability of the processes being developed.
- (b) AURI has access to methane from its manure digesters, which is becoming of potential interest as a feedstock for lactic acid and PHA's. AURI should contact NatureWorks/Catalysta and

emerging PHA players such as Mango Materials, Newlight and Oakbio to determine any synergism in supply of methane with their development plans.

- (c) Other opportunities for AURI to participate in bioplastics could be in the vegetable oil based polyols as plasticizers or flexibilizers.
- (d) AURI should continue extending their activities in natural fiber as reinforcement not only for bioplastics but for conventional polyolefins where biobased content is desired.
- (e) Soy based polyols are already making inroads into thermoset polyurethanes and will continue to do so. AURI is already involved in this area and should continue to form alliances with Cargill and USB and other players to help improve cost/performance. In addition, it is worthwhile for AURI to contact downstream users such as Ford Motor Company, John Deere and Nike in terms of their needs in soy based adhesives and coatings as well as compounders such as PolyOne who are looking for plasticizers to replace phthalates in PVC.