Biobased polymers keep textiles green

Growing demands from brand owners and consumers for fibres and textiles that are more environmentally friendly are now creating a huge market for biobased polymers produced using renewable feedstocks

Covestro

Covestro has produced biobased PU dispersions for textile applications

CYNTHIA CHALLENER VERMONT

The textile market covers a broad range of materials – both woven and nonwoven – used in applications ranging from clothing and apparel to interior and decoration textiles, technical textiles, medical textiles and safety and security products.

Consequently, the textile industry has a significant impact on the environment and has faced mounting pressure across the entire value chain from end users, consumers and non-governmental organisations to improve its performance with respect to sustainability.

One response to this need has been the development of biobased fibres from renewable raw materials. Many biobased polymers have been developed, including polyethylene terephthalate (PET), polyethylene (PE), polylactic acid (PLA), starch blends, biodegradable polyesters such as polybutylene succinate (PBS) and poly(butylene adipate-co-terephthalate) (PBAT), thermosets (epoxies, polyurethanes [PUR] and ethylene propylene diene monomer rubber [EPDM]) and cellulose acetate.

These accounted for 2% of global polymer production in 2013. Capacity for such renewable polymers is expected to increase faster than that of conventional polymers, leading to a 4% share by 2020, according the nova-institute, an organisation dedicated to advancing the use of renewable raw materials.

The textile industry share of worldwide biobased polymer production in 2013 is estimated by the group to be 18%, but expected to decline to 8% in 2020 due to more rapid growth in consumption of biobased polymers/plastics in the packaging sector (which is attributed to the fast growth of biobased PET).

In fact, nova-institute projects production capacity for PET to reach 7m tonnes/year by 2020, while production capacities for PLA and PHA will expand nearly four and tenfold, respectively, between 2013 and 2020.

Examples of leading companies producing biobased polymers and fibres intended for use in the textile industry include DuPont, NatureWorks, Invista, Corbion, Kaneka and Cathay Industrial Biotech.

DUPONT OFFERINGS GROW

DuPont makes *Sorona* (polytrimethylene terephthalate, PTT) biobased fibres (37% renewably sourced by weight) for carpet and apparel applications via continuous polymerisation of bio-PDO (1,3-propanediol), which is made from fermented sugars, and terephthalic acid (TPA).

Sorona production uses 30% less energy and releases 63% fewer greenhouse gas emissions compared to the production of nylon 6, according to Michael Saltzberg, global business director for biomaterials at DuPont.

He notes that growth in the adoption of *Sorona* is largely due to its unique performance properties, including softness, inherent stain resistance, stretch and recovery and durability; and secondly because of its renewably resourced content, which supports the performance. The company will be introducing new products in late 2016 or early 2017 that will expand *Sorona*'s colour palette capabilities and facilitate *Sorona*/natural textile blends.

DuPont Industrial Biosciences also announced in January 2016 that, in collaboration with Archer Daniels Midland Company (ADM), it has developed an efficient, high-yielding, low-cost method for the production of furan dicarboxylic methyl ester (FDME) from fructose. FDME is an attractive biobased raw material for the production of various polymers, such as polytrimethylene furandicarboxylate (PTF), a 100% biobased novel polyester produced via the copolymerisation of FDME and bio-PDO.

The two companies are planning to build an integrated 60 tonnes/year demonstration plant in Decatur, Illinois, to provide potential customers with sufficient product quantities for testing and research.

ChengHong Holding Group in cooperation with the Tsinghua University reported in 2014 that it was constructing a 50,000 tonne/year bio-PDO unit and 30,000 tonne/year bio-PTT plant.

The company noted that it uses crude starch and glycerine (a by-product of biodiesel) for the fermentation production of PDO and BDO (1,4- butanediol), respectively, and has gained independent intellectual property rights for its PDO and PTT processes. It also indicated that it was installing PTT spinning and fabric dyeing technologies.

Ingeo PLA from NatureWorks is used to manufacture a wide variety of textile products including apparel, furniture components, household materials, baby care products (diapers), personal hygiene goods and gardening supplies. *Ingeo* fibres are produced using 40% less non-renewable energy and generate 52% less greenhouse gases than conventional PET fibres, according to Robert Green, global segment lead, nonwovens and fibres with NatureWorks.

When compared to nylon 6, *Ingeo* fibres reduce non-renewable energy consumption by 67% and greenhouse gases by 81%, Green adds. "Most applications using *Ingeo* are driven by product performance. The major performance themes are moisture management, breathability and skin comfort for apparel and hygiene products, while for horticultural/agricultural applications, the renewable, sustainable and compostable attributes are highly desired," he notes.

NATUREWORKS BROADENS RANGE

NatureWorks continues to broaden the performance range with new resin grades for fibre applications and works closely with development partners to optimise processes and performance to demonstrate how *Ingeo* as a material can offer benefits.

For instance, customers are developing combinations of *Ingeo* products with natural fibres and other biobased resins to offer functional and sustainable products to the market.

Fitesa Simpsonville, for example, has developed the 100% renewable *Fitesa* 100% biobased spunbond nonwoven product made of *Ingeo* and Braskem's *I'm green* 100% biobased polyethylene. This won the 2015 RISE Durable Product Award from the Association of the Nonwoven Fabrics Industry (INDA).

CorbionPurac initially launched its biobased PLA resin portfolio for extrusion, thermoforming, injection moulding and fibre spinning in Europe in 2015, and for the North American market in May 2016. The company's new 75,000 tonnes/year PLA production plant is anticipated to start-up within the second half of 2018, and Corbion is currently testing, validating and selling pre-marketing volumes of PLA.

The product range includes PLLA (poly L-lactic acid) and PDLA (poly D-lactic acid) homopolymer resins for high heat, high performance, as well as standard PLA grades.

CHINESE POLYAMIDE DEVELOPMENT

Cathay Industrial Biotech, based in Shanghai, China, received $135m in additional financing in late 2015 that will be used to increase the production capacity at its existing Jinxiang facility and build a new production site.

The company manufacturers long-chain dibasic acids (LCDAs), including renewable dodecanedioic acid and 1,5-pentamethylenediamine (DN-5), a renewable diamine, that is polymerised with adipic acid to produce *Terryl*, a biobased polyamide 56, which serves as an alternative to nylon 6 and nylon 66.

The new polyamide has similar strength and wear resistance to traditional nylons, along with improved flowability, moisture absorbance, comfort, dyeability and antistatic and flame retardant properties due to disruption of some of the hydrogen bonds, which provides more sites for interaction with dyes and water, according to the company.

> **"Most applications using *Ingeo* are driven by product performance... attributes [that] are highly desired"**
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> **ROBERT GREEN**
> Global segment lead, nonwovens and fibres, NatureWorks

In addition, direct polymerisation melt-spinning provides significant cost savings. The company is currently investing an additional $500m to build a new production site for DN5, long chain diacids and biobased polyamides using its own raw monomer blocks in Xinjiang, western China.

The site is anticipated to be complete by May 2017 and will provide 50,000 tonnes/year of DN5, 100,000 tonnes/year of biopolyamides and double the current capacity for LCDAs.

Kaneka PHBH from Kaneka Corporation is a copolymer of a copolymer of 3-hydroxybutyrate and 3-hydroxyhexanoate and a 100% biobased polyester derived from renewable plant oils. The strain development and cultivation technology were achieved through a joint research effort with RIKEN, Japan's largest research institution.

Compared to PLA, PHBH is soft and has greater heat-resistance, biodegradability, hydrolysis resistance and water vapour barrier properties, according to the company. The production of fibres is a key end-use application.

Several other companies offer biobased fibres. INVISTA introduced a biobased version of spandex in May 2014. Approximately 70% by weight of the new *Lycra* bio-derived spandex fibre comes from dextrose derived from corn.

Japanese firm Toray manufactures biobased PET. Italian firm Fulgar launched in November 2015 'Evo by Fulgar", a 100% biobased high-performance fibre made of a biopolymer derived entirely from castor oil seed, which is grown in arid regions not suited for other forms of agriculture, according to the company.

Other firms have targeted the development of biobased additives for textile applications. Covestro introduced its *Impranil* eco range of waterborne, biobased polyurethane dispersions (PUDs) for use as textile coatings. The products contain 43% to 65% renewable content, offer performance that matches conventional products and can be used as drop-in replacements for existing PUDs according to the company.

BIOBASED COLLABORATION

Covestro collaborated with BioAmber, a supplier of biobased succinic acid, in the development of the *Impranil* eco line. The products recently (May 2016) won the Innovation Award Bio-based Material of the Year 2016, an award sponsored by InfraServ GmbH & Co. Knapsack KG, a service provider for the planning, construction and operation of plants and sites.

OrganoClick AB developed OC-biobinder, a biobased fibre-binding system used to make nonwovens and textiles stronger and stiffer. The company applies click chemistry to modify and change the properties of both naturally occurring cellulosic (wood, cotton, and linen) and manmade (viscose, polyester, polyamide) fibres. "We have developed technologies to add properties such as fire resistance, water repellency, fungal resistance and increased strength," notes CEO Marten Hellberg.

While continued growth of the market for biobased polymers used in fibres and textiles is expected in the short and long terms as expectations for both greater performance and sustainability increase, hurdles do remain for manufacturers of products manufacturers using renewable raw materials.

"Educating the market about these materials, the sustainability benefits that can be realised and the overall value proposition is one of the biggest challenges," says Green.

Limited manufacturing capacity for the production of biobased functional fibres is an issue for Hellberg. "Capacities need to increase further, which will also likely reduce the prices for biobased functional fibers," he observes.

Saltzberg stresses that success in the fibre/textile industries is dependent on not only having a competitive cost structure, but also acceptable properties, and preferably higher-performing properties. ■

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Natural packaging

Polylactic acid dominates the market for bioplastic packaging, but many other materials – including emerging ones – are also finding their niches

LOU READE LONDON

Natural materials have been used as the basis for plastics packaging for more than 100 years, since the introduction of cellophane in the early 20th century. However, the cellophane example is a bit of a red herring. The fact it was based on a renewable resource – in this case, cellulose, from wood – was largely coincidental. After its introduction, almost every other plastic used for packaging was derived from petroleum until polylactic acid (PLA) hit the market in the late 1990s.

PLA has become a well-established material for both rigid and flexible packaging. But while it is the most recognised bioplastic, it is not the only one.

There is now a vibrant bioplastics sector that has developed a host of other bio-derived plastics, including some from leading petrochemical players. Some of the materials, like PLA, are biodegradable – but all are derived from non-petroleum resources.

Probably the most commercially advanced is *Green PE* – a bio-derived version of polyethylene from Brazil's Braskem. The material is identical to standard polyethylene; the difference is the way in which it has been made.

Rather than being a by-product of petrochemical cracking, via naphtha, it is made from ethanol – which in turn is derived from sugar cane. Braskem says that 68,000 hectares of land are needed to grow enough sugar cane to make 460m litres of ethanol – which is then converted to ethylene and polymerised at its 200,000 tonnes/year production plant in Brazil. The plant produces three versions of polyethylene – HDPE, LLDPE and LDPE – which are all appropriate for packaging, and can be used in place of conventional PE.

Just recently, US personal care company Seventh Generation began using Braskem's biobased HDPE – blended with post-consumer recycled (PCR) material – for its 100oz laundry detergent bottles, which are produced by Consolidated Container Corp (CCC). The bottles were originally made from 80% PCR and 20% conventional HDPE, but the HDPE has now been replaced by Braskem's biobased version.

"This is a big step toward our 2020 vision of all packaging being made from recycled or biobased materials," says Derrick Lawrence, director of packaging development at Seventh Generation. "This collaboration with Braskem and CCC will help us improve the footprint and recyclability of our product packaging."

In addition, US office products company Samsill has produced a ring binder that incorporates 25% *Green PE*, while EEQO – a Dutch producer of natural cleaning products – is using self-adhesive labels based on *Green PE*.

TOUGHER THAN PET

Another emerging biobased polymer, PEF, is made by Dutch company Avantium at a pilot plant in Geleen. The facility can produce "several tonnes per year", according to Nathan Kemeling, director of business development for YXY – the arm of Avantium that is developing the material.

However, the company expects to finalise a joint venture with BASF over the summer that »

» will allow it to raise production as high as 50,000 tonnes/year, using a new plant to be built at BASF's site in Antwerp, Belgium.

"The main objective of the joint venture is to turn PEF into a commercial reality," he says.

PEF is a polyester that has superior properties to PET. He says the oxygen and CO2 barrier is 10 times that of PET, while the moisture barrier is at least twice as good. While PEF will not be able to replace PET across the board, its properties – including higher gas barrier and greater physical strength – will make it appropriate for special applications.

> **"Increasing attention has been placed on the development of food packaging material with antimicrobial and antifungal properties"**
>
> **THIAN ENG SAN**
> Researcher, National University of Singapore

One possibility is to replace existing multi-layer films – which use an expensive barrier material such as EVOH or nylon – with a mono-layer PEF film. This would simplify the production process, and help to reduce costs.

Alternatively, a multi-layer film that combines PEF with barrier materials such as EVOH could compete with some metallised films, he says.

"The added bonus here would be transparency," he says. In collaboration with a biaxial film company, Avantium has also produced a range of oriented – or stretched – packaging films on a continuous line. Oriented films are widely used in the packaging industry. The project has shown that PEF could be produced on existing machinery, which is used to make oriented polypropylene (PP) or PET film, for example.

Avantium's original work in PEF was for bottles. It has produced prototype bottles for Coca-Cola (for carbonated soft drinks), Danone (sparkling and flavoured water), and Austrian packaging company Alpla – for packaging beer.

"A plastic beer bottle is a huge challenge," says Kemeling. "It must protect against oxygen, CO2 and moisture, and allow in-bottle pasteurisation." PEF is capable of meeting these criteria, he says – and could also allow hot filling. In future, Avantium is planning to produce a PEF beer bottle in time for the Japan 2020 Olympics.

The company also has an agreement with Mitsui in Asia, in which Mitsui distributes relatively small amounts of PEF from Avantium's pilot plant production.

"Mitsui is looking to develop the market for PEF in Asia," he says. Once PEF is fully commercialised, Avantium plans to license the technology to interested partners.

PRECURSOR SEARCH

The search for precursors is spreading ever-wider. In addition to the existing commercial and near-market technologies, there are many research-level projects that could lead to alternative biobased plastics. Many of these approaches focus on using waste or discarded products as the feedstock for packaging products.

Researchers at the National University of Singapore (NUS), for instance, have developed a food packaging material that combines chitosan-based composite film with grapefruit seed extract (GFSE). The material can slow fungal and bacterial growth, doubling the shelf-life of perishable foods such as bread.

Chitosan, a biodegradable polymer derived from the shells of crustaceans, has inherent antimicrobial and antifungal properties. GFSE is an antioxidant and has antiseptic, germicidal, anti-bacterial, fungicidal and anti-viral properties, say the researchers.

Thian Eng San and Tan Yi Min, from the Department of Mechanical Engineering, spent three years formulating the composite film – which has a mechanical strength and flexibility comparable to traditional polyethylene film packaging. "Increasing attention has been placed on the development of food packaging material with antimicrobial and antifungal properties, to improve food safety, extend shelf life and minimise the use of chemical preservatives," says Thian. "Consumers are also demanding that packaging materials be formulated from natural materials that are environmentally friendly and biodegradable while improving food preservation."

The new film also blocks ultraviolet light, slowing the degradation of food through oxidation and photochemical deterioration. Laboratory tests showed that the shelf-life of bread samples packaged with chitosan-based GFSE composite films was double that of those packaged using conventional packaging films.

Thian and Tan will conduct further studies to improve the technology. They will look at the degradability of chitosan-based GFSE films, as well as carrying out an accelerated shelf life study to examine the extent of microbial growth and quality changes during storage of various food products.

Many other potential precursors are also under consideration (see box).

BIO-ENGINEERED PLASTICS

There are other ways to make bioplastics. All these examples are effectively conventional chemical processes, using a renewable raw material in place of petroleum. Other technologies use bio-engineering techniques to produce bioplastics as a natural by-product. This is the case with polyhydroxyalkanoate (PHA) and its variants.

In a microscopic equivalent of these chemical processes, genetically modified organisms convert sugar into PHA – which is then harvested using solvent extraction.

One leading producer, US-based Metabolix, recently developed an amorphous grade of PHA, which is more rubbery than its crystalline version. The company is already seeking FDA clearance for the material in food contact applications. It is also working with customers interested in a PHA-modified PLA for thermoformed transparent clamshells used in food service and consumer packaging.

At the same time, Bio-on of Italy is forging ahead with its plans to develop PHA from a range of sustainable resources. It is planning a 5,000 tonne/year plant in Italy using glycerol (a by-product of the biodiesel industry), and has separate plans for a 10,000 tonne/year plant in Brazil, powered by sugar cane by-products.

In a nod to the past, it is using the original bioplastic precursor – wood – to make PHAs. In a $1.4m research project with the University of Hawaii, it plans to use lignocellulosic materials (wood processing waste) and domestic or agricultural waste as the raw material. Wood, it seems, is still good. ■

LOU READE LONDON

NEW POLYMER SOURCES SHOW PROMISE

CONVENTIONAL PLASTICS generally have one source: oil. Until recently, sources of bioplastics were limited to corn and sugar cane, but researchers are casting their net more widely in search of new plastics precursors. Some recent examples include:

■ **Legumes:** by-products from crops like lentils, peas and broad beans could form the basis of new packaging materials. Researchers in the pan-European Leguval project have already identified barrier coatings from pea proteins, for example, and are on the hunt for other raw materials that could form the basis of new bioplastics

■ **Animal proteins:** New Zealand-based Aduro Biopolymers – a university spin-off – is already producing a material called *Novatein*, which is made from blood-meal. At the same time, the pan-European Wheylayer project, which developed barrier biopolymer coatings from whey proteins, is now in its commercialisation phase.

■ **Soybeans:** Researchers at Iowa State University in the US are ramping up production of a biopolymer based on soybean oil, at a $5.3m pilot plant. Throughput is around 1,000 lbs (455kg) per day. The polymers will be tested for use in applications including packaging materials. ■

Biobased adds to circular economy

The EU's Circular Economy Package sets some stiff targets for materials re-use and recycling. Biobased chemicals have a vital role to play and the industry is generally positive on the EU's approach

JONATHAN LOPEZ LONDON

The EU wants to lead the way in recycling and waste management by achieving a "circular economy" by 2030. The disparate realities across the 28 member states, however, suggest the deadlines should be taken with a pinch of salt.

In December 2015, the European Commission issued its Circular Economy Package covering all phases of industrial activity: from production and consumption to waste management and the market for secondary raw materials. The most ambitious aspects come in waste reduction and management, and recycling. These set up an EU-wide target to recycle 65% of municipal waste by 2030 and 75% of packaging waste by the same year.

The central idea behind the circular economy will require industrial sectors to leave behind the development model in place for the last 200 years and jump to the next phase in which reuse and service-life extension of goods become a key strategy to prevent waste and use energy more efficiently. As it has been called, to "dematerialise the industrial economy".

"Owning a good makes sense if that good increases in value – owning a house makes sense, owning any disposable good doesn't. Therefore, we should rent it," says the man behind the circular economy idea, Swiss architect Walter Stahel.

EU environmentalists and industries which are to benefit the most from the package have welcomed the Commission's initiative. Some voices, however, have argued the pressure from trade groups – which include some of those companies to lose out, mainly fossil fuel-related industries – made the executive, presided over by Jean Claude Juncker, water down its initial proposals to make the transition more bearable for them.

"I think this package could be a game changer for Europe. If you look at all the developments in the industry going on around the circular economy in terms of job creation by creating new business opportunities while also cutting emissions, that's a big deal," says Pieter De Pous, policy director at the European Environmental Bureau (EEB).

Biobased industries across the EU have welcomed that, for the first time, a package of this nature has established a clear link between the circular economy and the role their manufacturing sector could play in it. They already have a large base on which to build.

LARGE BIOBASED ECONOMY'

According to the Bio-based Industries Consortium (BIC), the European bioeconomy achieved a turnover in 2013 of €2.1 trillion and employed some 18.3m workers across the region. According to the same study, the main biobased sectors in the EU are agriculture, forestry and fishery, which amount to 58% of the total. Equally, BIC highlights how the biobased chemical industry has increased its share within the sector from 5% in 2008 to 6% in 2013.

Kristy-Barbara Lange, deputy managing director in charge of regulatory affairs at trade group European Bioplastics, says the Commission's package is a good start but more ambitious targets could have been set. However, she celebrates the fact that for the first time a package of this type includes allusions to the bioeconomy as a key element to develop a circular economy.

"This current package actually promotes mandatory biowaste collection, and this is very important for our industry because some bioplastics can also be biodegradable. By 2020, the infrastructure to do this should be set up," says Lange. "Connected to that, it is important to have within the package an inclusive biobased definition as well as a call for organic recycling – you don't want just to collect the stuff, you want to do something with it."

Within the package, the Commission proposes a binding landfill target to reduce landfill to a maximum of 10% of municipal waste by 2030 and a ban on landfilling of separately collected waste as well as the promotion of "economic instruments to discourage" landfilling.

According to the Commission's figures, in 2013 the EU's total waste generation stood at 2.5bn tonnes but around 65% of it (1.6bn tonnes) was not reused or recycled. Landfills continued to be an important instrument to dispose of waste, with the high environmental costs associated to that.

> **"We are talking about a paradigm shift – not just minor adaptations"**
>
> **HARTWIG WENDT**
> Executive director for sustainability, Cefic

Out of the 1.6bn tonnes of waste which were not reused, the Commission estimates around 600m tonnes of them could be recycled or reused, and that is where the circular economy initiative would take centre stage.

The EU, however, will have to think about what to do with the remaining 1m tonnes which cannot be recycled. Ways of storing or destroying that waste without harming the environment will need very imaginative and technologically advanced solutions.

However, one of the more pressing aspects the Commission is yet to develop a more ambitious package for is the phasing out of hazardous chemicals. Without that, a true circular economy will not be achieved. The action plan »