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A few weeks ago I stumbled over a series of Internet news items with broad headlines about a (well-known) laptop producer, now offering green biodegradable notebooks. The news read something like this: “... as part of its green initiatives, Brand-X said it built the two new models to be free of PVCs (polyvinyl chloride) and BFRs (brominated flame retardants). PVC is a cheap but durable plastic that has been criticized by Greenpeace for not being biodegradable and for emitting toxic substances into the environment” (see www.bioplasticsmagazine.de/201003).

Well, that made me think: My grandma’s chamber pot (enamel) is definitely free of PVCs and BFRs, both of which Greenpeace has criticised for NOT being biodegradable.

- Conclusion: my grandma’s chamber pot is biodegradable.

One fool (who now is no longer identifiable) publishes this, and is followed by a whole host of short-sighted ‘online journalists’ who are delighted to disseminate the ‘eco-friendly’ news. Now, if it is published on lots of different websites, it must be true...

Anyway, this is why you will not find this particular laptop in our magazine. Instead, this issue is again the thickest ever and offers a whole lot of serious information. We cover ‘injection moulding’ as one of our editorial focus subjects.

Even if ‘natural fibre materials’ often use fossil-based plastics as a matrix, we consider this family of materials as quite interesting. Natural fibres can enhance the properties of a compound and they also contribute to reducing the use of fossil resources. In addition, there are a lot of other innovative approaches, and not only into the use of matrix resins from renewable resources.

In the ‘Basics’ section we try to explain polyamides and different ways to generate such plastics from biogenic sources.

I hope you enjoy reading this issue of bioplastics MAGAZINE.

Yours

Michael Thielen
Injection Moulding

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PLA Beverage Bottle Presented in Austria 57
European Inventor Award for Tecnaro

TECNARO GmbH from Ilsfeld, Germany received one of the most prestigious international awards, the European Inventor Award 2010 (in the SMEs/research category). Nominated from among more than 1,000 inventors and patent applicants Tecnaro got the award for their Arboform, an environmentally friendly material replacing petroleum-based plastics in many industrial applications and offering further significant advantages for example being biodegradable and pleasant to handle as a finished product (wood).

The award was handed over in Madrid by Alison Brimelow, President of the European Patent Office. Prince Felipe und Princess Letizia, heir apparents from Spain patronized the award in 2010 and congratulated the winners.

Awarded are inventors and inventions which contribute significantly and sustainable to technical progress and due to this to the increase in European economy. Key factors were innovation, already achieved success in the market and future potential.

The company Tecnaro (the name abbreviating the German expression for Technology of renewable resources) is a Fraunhofer spin off and developed Arboform about twelve years ago. The material is based on lignin, (a major component of wood), various natural fibers such as hemp and flax as well as natural additives. Besides cellulose, the wood component lignin is the second most common organic material on earth, about 20 billion tons of lignin being formed each year by photosynthesis. This ensures an almost infinite supply of lignin as a raw material without competing with food products. Approximately 60 million tons of lignin are produced annually as a by-product within the Cellulose industry, mainly in the production of paper. Lignin may even be extracted from tree bark, sawdust or straw. The mixture of renewable resources is processed further through special procedures to form granules which can be used for various products manufactured by conventional plastic fabrication techniques.

The thermoplastic material offers not only technical and economical advantages but also ecological benefits. With Arboform, industry gains independence from petroleum as a raw material, it can easily be recycled, and even composted or burnt without releasing additional CO₂. This explains the very strong interest within the plastic and wood processing industry in Arboform. Particularly the automotive industry is fascinated by this new environmentally friendly material: It looks like wood, it feels like wood, but can nevertheless be processed easily into a wide variety of three-dimensional shapes, e.g. for car interior design. Companies involved in the packaging business as well as manufacturers of furniture, toys, shoes and music instruments have become established users of the material.

Patent Dispute going on

On Friday 16 April last, the Paris Law Court issued the first-instance sentence in the case brought by Novamont against the German company Biotec and certain companies of the French group Sphere, respectively, the manufacturer and distributors of certain starch-based products which, it was alleged by Novamont, infringed its patents protecting first generation Mater-Bi.

The Court found two Novamont patents to be fully valid and a third patent to be partially invalid while also finding that Novamont had not provided proof of the infringement. Not entering into the merit of the case, the Court noted that the analyses on samples of the products of the summoned companies had not been conducted in a two-party process.

Novamont greeted with satisfaction the fact that its important patents were considered valid and remains convinced that they will be declared to have been infringed when it comes to examining the aspects of substance of the dispute. Novamont will therefore pursue with the greatest conviction its actions against the infringement of its patents, and in particular those currently pending before the Italian Courts.

Novamont CEO, Catia Bastioli, stated: “This ruling confirms the validity and worth of our intellectual property and encourages us in our efforts to produce and protect it. We are convinced that, once the formal aspects have been cleared up, our exclusive rights will be enforced in France as well.

After the launch of the first second generation Mater-Bi products, protected by a host of patents, we shall continue with our investments to make third generation mater-Bi industrially available.”

However, according to recently published online-news, Novamont is going to to appeal against the initial judgment of April 16. The news said that Novamont was to pay 50,000 Euros each to Biotec and Sphere.
Bio-based Material of the Year - Awards

There is no judging panel, it is the group of conference delegates who vote for the winners of the competition ‘Bio-based Material of the Year’ at the 3rd International Congress on Bio-based Plastics and Composites. This year it was at the renowned HANNOVER MESSE in Germany. The award was presented for the third time by the nova-Institut and sponsored by the machine manufacturer Coperion.

The coveted 1st place was won by the German company Propper GmbH for their material Proganic®, based on Polyhydroxyalkanoate (PHA), Carnauba Wax and natural mineral fillers (see details on page 14).

Runner-up was GreenGran B.V. from the Netherlands with their material GreenGran, produced in China. The natural fibre reinforced plastic for injection moulded applications is being introduced on page 34.

Henkel AG & Co. KGaA took third place with its PLA-based material, ‘Arctic’, from which office supplies will shortly be produced. In Hanover the Arctic material was presented in its application in the ‘Pritt ECOmfort Correction Roller’ (see article on page 44).

All three awardees attest to the fast development of bio-based plastics and composites. Whereas in the recent past the area of bioplastics was particularly dominated by short-life applications in the packaging industry, where the biodegradability was the focus, the bio-based plastics and composites of our three winners are used in durable applications. The focus is now on “bio-based”, and biodegradability remains only one possible end-of-life option. MT

FDA Approval for Mirel

Metabolix, Inc. and Archer Daniels Midland Company announced that their Joint Venture Telles received U.S. Food and Drug Administration (FDA) clearance for the formulated products Mirel™ F1005 and F1006, food contact injection molding grades for use in food contact applications.

Mirel F1005 and F1006 grades are now cleared for use in non-alcoholic food contact applications. The conditions of use range from frozen food storage to boiling water up to 100°C, including microwave reheating. Mirel is suitable for a wide range of injection molded food service and packaging applications including caps and closures, and disposable items such as forks, spoons, knives, tubs, trays, and hot cup lids. The clearance also includes products such as housewares, cosmetics and medical packaging (see detailed article on page 16).

“With the Clinton plant now in operation, and this FDA clearance, we now can move forward with brand owners’ requests to use Mirel in their injection molded food packaging applications,” stated Richard Eno, CEO of Metabolix. “These applications, which currently consume billions of pounds of petroleum-based polymers per year, offer considerable opportunity for growth of our biobased, biodegradable polymer, Mirel.”

Telles engaged Intertek to help develop the full dossier for this food notification submission. Intertek is a leading provider of quality and safety solutions serving a wide range of industries around the world.

www.mirelplastics.com
News

New VP Sales and Marketing at Cereplast

Cereplast, Inc, El Segundo, California, USA, manufacturer of bio-based, sustainable plastics, recently announced that it has appointed Robert (Bob) Findlen as senior vice president of global sales and marketing to lead the Company’s sales team.

Bob Findlen brings over 25 years of sales, marketing and management experience and has a demonstrated track record of success combined with considerable experience in the conventional plastics and bioplastics industries. He has served with top multinational plastics conglomerates in increasingly responsible executive roles, including General Electric, LNP Engineering Plastics, and most recently at Metabolix, Inc., where he was Vice President of Sales and Marketing. He will be responsible for overseeing a strong and seasoned team of sales executives while building and maintaining customer relationships and strategic partnerships.

“I am confident that Bob’s experience in leading, managing and developing sales teams will have a strong impact on our aggressive expansion plans,” said Frederic Scheer, founder, chairman and CEO of Cereplast, Inc. “Our new facility in Seymour, Indiana, will be capable of producing roughly 100 million pounds (45,000 tonnes) of bioplastics per year. Based on Bob’s accomplishments and track record, we are confident that we will be able to meet the initial demand he is expected to generate. Bob was extremely successful at building a robust pipeline of new business at Metabolix and is a significant addition to our management team. I am excited to have him join us.”

Mr. Findlen stated, “Frederic’s vision and hard work is opening doors for Cereplast in 2010 and creating tremendous new opportunities. He is truly a pioneer in the bioplastics industry and understands the significance and impact of this alternative technology in the 21st Century. I look forward to working with Frederic in expanding the use of Cereplast resins across many different market segments, resulting in increased sales and growth performance for the business.”

First PLA Pilot Unit in Europe

Futerro, a 50/50 joint venture established in September 2007 by Galactic and Total Petrochemicals, recently announced the inauguration of its bioplastics production unit in Escanaffles, Belgium. Supported by the Walloon Region through the Marshall Plan, the purpose of this unit is to develop state-of-the-art technology for the production of Polylactic Acid (PLA) bioplastics from renewable vegetable sources developed by the two partners.

By bringing this plant on stream, Futerro has become the first producer of this type of bioplastics in Europe. Clean, innovative and competitive, this technology comprises two main steps. The first step is the preparation and purification of the monomer, lactide, from lactic acid, which is obtained by fermenting sugar, here mainly from sugar beet. Other vegetables such as sugar cane, corn and wheat can also be used to produce lactic acid. Such renewable resources as well as other biomass from forest and agricultural waste are also conceivable in the future. In the second step, the polymerisation of the monomer, the PLA in form of plastic granules is obtained.

The pilot unit, which has a capacity of 1,500 tonnes per year and represents an investment of 15 million Euros, will be used to test and improve the successive steps in this technology. Futerro is now able to produce a complete range of products from lactic acid, including lactide, and PLA oligomers and polymers. They will be used by the packaging industry, primarily food packaging, and in sustainable applications.

Futerro
www.futerro.com
www.lactic.com
www.totalpetrochemicals.com

MT

www.cereplast.com

bioplastics MAGAZINE [03/10] Vol. 5 7
A comprehensive report entitled ‘The state-of-the-art on Bioplastics 2010’ written by Jan Th. J. Ravenstijn MSc, has been available since January of this year. The author holds an MSc Degree in Chemistry and Chemical Engineering from the Delft University of Technology in the Netherlands. With more than 30 years experience in the chemical industry and after holding a post as Visiting Professor for Biopolymers at the Eindhoven University of Technology in 2009, he became a consultant to international biopolymer companies in America, Asia, and Europe.

In his report, covering more than 100 pages in A4 format, Ravenstijn examines the revolutionary growth of bio-based monomers, polymers, and plastics, the changes in their performance, and the wide variety available to the entire global plastics market. The report also reviews and discusses trends, contentious issues, technologies, products, markets, manufacturers, investment plans, performances, needs, expectations, and new opportunities, including the potential collaboration of the agricultural industry with the polymer industry to create a new value chain.

The report is extremely well structured and begins with a comprehensive introduction into the subject of bioplastics, including explanations of the most commonly used terminology. The whole book is written in intellectually sophisticated, yet easy-to-read and easy-to-understand English. When I started to read the book I couldn’t put it down until I had finished it [It’s a real ‘page-turner’, like a thrilling novel]. I do admit however that was on a transatlantic flight, but I actually missed the movie …!

After a comprehensive introduction of the ‘main’ bioplastic materials, including the very basics of PLA, PHA, starch etc, the report names the major players in the industry, discusses potential applications and does not conceal any of the drawbacks or challenges.

Whilst Jan Ravenstijn’s writing is, from time to time, quite scientific (which for those who understand terms like ‘12-hydroxy-9-cis-octadecenoic acid’ is certainly highly informative) he also entertains the rest of us with passages enriched by a little history. PLA, for example, goes back to 1845 … . He supplies useful background information, such as details of the European legislation on CO₂ emission reduction for automobiles step by step until 2020, and much more.

Although the author clearly states his position when it comes to questions such as ‘Composting - where it really makes sense and gives added value’ or ‘the use of genetically modified crops’, he is not so clear about the so called oxo-biodegradables.

All in all the report is a really useful and informative publication. It covers all the basics, the materials, the major players and in addition it deals with questions such as:

- Will bio-based polymers provide new functionalities or will they simply replace existing fossil resource based polymers?
- Why is a successful market entry by bio-based polymers more likely today?
- Which technological advances are required for bio-based polymers?
- What is the importance of the interface between White Biotechnology and Polymer Material Technology?
- What are the social, economic and technical issues and how are they to be addressed?

For more information or to purchase the report visit the bioplastics MAGAZINE bookstore at www.bioplasticsmagazine.de/books
PSM® low-carbon materials and biodegradable materials

Originating from nature and back to nature.

Application fields:

These biodegradable materials are used in various fields such as household appliances, stationery, toys, and packaging products. They are suitable for injection molding processes, as well as extrusion, foaming, and film-making machines.

PSM environmental materials include PSM low-carbon materials and biodegradable materials, which can replace traditional plastics to manufacture all kinds of one-off and nondurable products.

The CO2 emission is 1/10 compared with that of PP. The electricity energy consuming by each ton PSM materials is 490 degree, equal to 196kgs standard coals, while each ton common plastic (such as PP) consumes 2200 degree electricity equal to 900kgs standard coals.

Certification:

- China Environmental Product Label
- OK Biobased
- Japan Bio-based Material Certification
- OK Compost
- DIN
Despite tight corporate travel budgets, 31 exhibitors and more than 300 people from 30 countries attended Innovation Takes Root 2010, the international bioplastics conference hosted by NatureWorks in Dallas, Texas, USA. Meals and the two evening receptions offered excellent opportunities to make or renew connections and to discuss the many interrelated aspects of sustainability, bioplastics processing, and marketing products with low environmental impacts.

**Successful integration of PLA into existing manufacturing facilities**

In a lively, interactive Q&A session, five industry leaders dispelled prevailing myths around processing Ingeo™, demonstrating with a number of examples of implemented solutions that the equipment industry has moved past the exotic new material phase. Topics covered included, running Ingeo sheet, crystallizing and drying, screw and cooling mandrel technology, biaxially oriented films, and agglomeration reclaiming technology.

**New PLA-based product developments**

A cross section of leading brands and manufacturers showed the momentum that is now behind the industry drive toward offering high quality consumer products and packaging.

Representatives of Spartech discussed new higher heat resistant sheet stock. Sony described its push to include bioplastics and decrease the fossil carbon content of its plastic components, Clear Lam Packaging not only spoke about its latest portfolio of new products, but also the results of a new consumer study in the USA demonstrating consumer awareness around the renewable theme. Fabri-Kal showed Ingeo cups and discussed production, while Sommer Needlepunch shared inside details on the development of the Ingeo exhibition-grade carpet used at Copenhagen’s COP-15 conference, and subsequently recycled into lactic acid (see bM 01/2010)

**Additives and blends approaches to tailoring PLA performance**

Two technical tracks explored how the latest technologies from leading industry compounders and additive suppliers are taking Ingeo and other bioressins to new levels of performance.
The compounders PolyOne, Teknor Apex, and RTP described approaches for achieving engineering resin properties with bioplastics through compounding. PolyOne presented its new reSound™ products line which contains a minimum 30 wt % PLA, PHB, PHBV, etc. for applications requiring improved sustainability and higher engineered performance. Teknor Apex described thermoplastic starch (TPS) technology for Ingeo modification, and RTP described compounded Ingeo or biobased PA formulations (32-80% biocontent) as offsets to HIPS, PC/ABS, 30% glass fiber reinforced polypropylene, or polyamide composites.

For those interested in 100% bioplastic blends, PHA producer Tianan Biologic compared properties and potential of PHBV/Ingeo and PHBV/EcoFlex® formulations, Industry Suppliers Takemoto, Sukano, and polymer producers BASF and Arkema highlighted technologies to improve the property and processing performance of Ingeo products. Enercon detailed its latest in surface treatments for improved adhesion of UV Flexographic inks to PLA substrates.

NatureWorks’ Jed Randal provided the first public details of the formulation behind the new injection molding grade of Ingeo 3801X.

Advances in PLA fibers and nonwovens

US Pacific, Alhstrom, and the University of Tennessee shared the newest advances with Ingeo nonwovens in spun-bond and melt-blown applications such as hygiene, filtration, and agriculture. Fiber finish producer Ghoulston presented the latest in Ingeo fiber surface modification developments, while NatureWorks’ longest standing Ingeo fibers ‘Master Licensee’ partner, Fiber Innovation Technologies (FIT), shared recent developments in how FIT tailors fiber structure to customer requirements.

Cradle-to-cradle

A highly interactive panel session, moderated by the Sustainable Biomaterials Collaborative’s Brenda Platt, looked at recovery from two angles — both composting, and reformulating post consumer and post industrial PLA back into lactic acid. Galactic (Europe) and BioCor (USA) discussed their businesses based on the model of lactic acid recovery from a variety of post consumer and post industrial polylactide residual sources.

Frito-Lay gave an overview of its extensive composting research for the compostable Sun Chip snack bag, while Canadian manufacturer Dyne-a-Pak introduced the successful development and market introduction of its compostable Ingeo-based alternative to polystyrene foam food packaging. California State Chico’s Dr. Joe Greene discussed the holistic approach the school has taken to analyzing claims and performance of biobased packaging and food service ware.

The business case for going green

NatureWorks President and CEO Marc Verbruggen closed the conference, sharing his perspective with the audience on “keeping the innovation cycle going.” Describing the outlook for Ingeo in the next several years, Verbruggen noted that variable cost parity between Ingeo and incumbent materials is within range, and that the increasing economies of production scale within the supply chain downstream of NatureWorks will help improve efficiencies and cost for all sales channel partners.

As proof points, Verbruggen highlighted the breadth and increasingly mainstream nature of the portfolio of Ingeo-based products now available to consumers; the third party interest and investment is transforming options for after-use treatment of bioplastics into new businesses; and the breadth of consumer communications now evident in the market as a key indicator of awareness and market penetration.

Presentations are available upon request from NatureWorks.

[www.natureworkslc.com](http://www.natureworkslc.com)  
[www.innovationtakesroot.com](http://www.innovationtakesroot.com)
A major driver for our collaborative activities, which we have named Bio-Moulding and Design, is our perception that many bio-based plastics - similar to but partly different from the currently known plastics - open up new product opportunities as well as sustainable life cycle optimisation, beyond mere material replacement. Most of the potential opportunities still need to be developed. In addition to impressive ongoing materials-related activities world-wide, we consider it necessary to contribute with product-related work by combining our manufacturing and design competences. Most of our activities concern injection moulded products. A significant part of existing bio-based plastics applications is for foils, bags, trays, bottles and other packaging items. Injection moulded bio-based plastic products also exist, although the full potential and broad applicability of injection moulding has only partly been utilised until now. A challenge is that injection moulding is traditionally most suited for large production volumes, not matching the current availability of most bio-based plastics grades. Certain mould making advancements, fortunately, make lower production volumes economically feasible. These and other less explored opportunities deserve further investigation.

Our impression is that the majority of designers, processors and other applicators are not as fully up-to-date on materials developments as the materials experts who are directly involved. A current limitation for applying bio-based plastics is that they are often seen as substitutes for existing plastics in existing products. This may be sufficient for materials such as bio-based PEs and PPs. For unique bio-based plastics such as PLAs and PHBs, however, there may be many more opportunities for design and application. As an example, the very low thermal shrinkage of some grades during processing may be used as an opportunity for product geometries that could not be achieved satisfactorily with traditional plastics: many design guidelines for injection moulded products were created to minimise the negative effects of shrinkage. A typical material characteristic thus becomes an opportunity for new designs, rather than a limitation in existing moulds. The challenges for low-shrinkage materials can be addressed in new moulds by adjusting draft angles and the ejector system.

Our planned experiments, using several PLAs and PHBs, include iterative evaluation of processing windows concurrently with optimisation of moulding processes and moulds, as well as evaluation and optimisation of product quality as assessed by mechanical testing. The objective of these activities is a complete set of moulding-related and geometry-related design guidelines for bio-based plastics products. We have started exploring processing windows with existing moulds and mechanically testing moulded specimens and specimens from moulded products. By
using real products rather than standard specimens only, we can quantify the practical consequences of different geometry details of products and gates, and flow weld lines, as well as estimate notch sensitivities.

Multi-material or hybrid moulds offer opportunities for low-volume injection moulding. Specific details in hybrid moulds can be obtained by rapid layer-wise manufacturing principles as with rapid prototyping. We thus plan to generate different gate and product geometries at low cost within a short time. We have compared conventional and hybrid moulds for tensile-impact specimens (figure 1), one of them with a cold flow weld line. We maintained the restrictive gating and limited draft, which should be adjusted in the next round of experiments. The main disadvantage, for the modified PLA we used was extended melt residence time in the plasticator due to lower cooling capacity in the mould insert. This can be improved with the concept of conformal cooling, achieving fast cooling with rapidly manufactured mould details.

We have tested many more combinations of materials and geometries. An interesting set of mechanical test results is shown in figure 2. A robust processing window with the existing mould was obtained only for HIPS, PP and PLA grade M106. The latter gave good results in product regions without flow weld lines, but less than PLA grade 2002D at the weld line, most likely because of the higher degree of polymerisation and more homogeneous structure of the latter. Future work will include the optimisation of processing with modified moulds and further impact testing at different temperatures.

The essence of our work is that we focus on contributing to new product opportunities for the near future. The latter is typical for integrative design approaches. A future-oriented vision is that product design should evolve into life cycle design. In this vision the concept of renewability will not only apply to materials, as for bio-based plastics, but to all combined material flows in societies. An excellent MSc graduation project focussing on such strategic challenges was completed in 2009. Based on the project’s findings, some approaches to design task integration into value chains were proposed. These approaches are aimed at broad implementation of life cycle thinking to achieve profitable sustainability. Details will be published in the near future.

With our work we aim to help broaden the scope of bio-based plastics applications, anticipating a more sustainable future context in which the benefits of bio-based plastics will be more fully expressed than at present.

www.abb.nl
www.cpmt.eu
http://english.hogent.be/
http://io.home.tudelft.nl/en/

Fig. 1: Stereolithography mould insert built into mother mould

Fig. 2: Best pendulum impact test results at room temperature of specimens from a cup holder part made from a HIPS, a PP, and four PLA grades (* = no (full) break)
At the recent International Congress on Bio-based Plastics and Composites, the first prize of the Innovation Award for Bio-based Material and Application of the Year 2010 was awarded to PROGANIC® (see p. 6). The award by the nova-Institute and sponsored by Coperion GmbH recognises the outstanding work undertaken by Propper® GmbH in bringing Proganic to the customer and to Industry.

Company History

Proganic is the brainchild of Propper GmbH & Co. KG, based in Rain am Lech, Germany. Established in 1948 the company is today a leading specialist in plastic gardening and household items which are sold worldwide and are now available in Proganic. Propper produces over 95% of its own products at its ultramodern production facilities in Zittau, Germany. It is widely known for its original design, ‘made in Germany’ quality, and its outstanding value for money. The best example of Propper’s flexibility and receptiveness to innovation is its new bioline, introduced worldwide in the spring of 2010.

Proganic History

“We started looking for alternatives to conventional plastic as a request from some of our key accounts back in 1990,” says Oliver Schmid, Managing Director of Propper, “the first experiments with primarily wood based plastic compounds were not so successful. There were problems in maintaining form, water resistance and overall cosmetic appearance.” These initial results made the company realise that there would be an immense challenge ahead and set itself the following exacting criteria for a bio based alternative to conventional plastic for its own products:

- 100% natural ingredients
- Petro chemical free
- Palm oil free
- Compliant with all existing injection moulding machinery and mould tooling
- Water resistant
- Home compostable
- UV stable
- Low shrinkage on finished product
- Comparable strength and durability to existing products
- Cost effective.

What is Proganic

Proganic is a bio polymer based on PHA (Polyhydroxyalkanoates), as well as a combination of renewable vegetable oils, waxes and natural minerals which provide sealing and water resistance. It can be used as a replacement for a variety of thermoplastics including PP and ABS. Technically it is most comparable to ABS plastic.

Proganic is tested for its ‘ultimate aerobic biodegradability of plastic materials in an aqueous medium’ according to ISO 14851 (by measuring the oxygen demand) and ISO 14852 (by analysis of evolved carbon dioxide). It is home compostable in both open and closed composters at 20°C. It conforms to the European Norm 71, Articles 3 and 9 (toys) it also conforms to the requirements of the American Food and Drug Administration (FDA) for use in the food and beverage industry. Proganic products currently available directly from Propper include watering cans, flower pots, self adhesive hooks, egg cups and spoons, strainers.
Based Compound
by Michael Thielen

Processing

Proganic can be injection moulded as well as ultrasonically welded and is therefore suitable for a variety of products. It has been successfully extruded into filaments as thin as 120 μm making it suitable for all types of brushes. The extrusion blow moulding process is under development, early indications look promising.

Proganic should be pre-dried at 50°C for at least 2-4 hours in order to avoid ‘cloud formation’ on the surface (water content before processing: less than 300 ppm). Recommended storage conditions are dry and below 25°C. The residence time in the injection moulding machine at processing temperature should not exceed 30 minutes. Otherwise the plasticator must be purged with polystyrene or other cleaning granulates. The same purge procedure is recommended after running Proganic before material changeover. See the separate box for more processing parameters.

<table>
<thead>
<tr>
<th>Screw design:</th>
<th>standard 3 zone screw, standard non-return valve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nozzle:</td>
<td>open or closed</td>
</tr>
<tr>
<td>Dosing speed:</td>
<td>works in conjunction with frictional heat and cycle time</td>
</tr>
<tr>
<td>Dynamic pressure:</td>
<td>approx. 0 – 10 bar (hydraulic)</td>
</tr>
<tr>
<td>Injection pressure:</td>
<td>so high that the cavity takes between 2 – 5 seconds to be filled (slower injection means reduction / avoidance of shrink marks)</td>
</tr>
<tr>
<td>Holding pressure:</td>
<td>high, approx. 20 – 100 bar (hydraulic)</td>
</tr>
<tr>
<td>Holding pressure time:</td>
<td>long, approx. 2 to 5 sec. (avoids shrink marks)</td>
</tr>
<tr>
<td>Tool temperature:</td>
<td>10°C – 30°C (depending on flow path lengths)</td>
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<tr>
<td>Hot runner:</td>
<td>170°C – 200°C</td>
</tr>
<tr>
<td>Cylinder temperatures</td>
<td>Nozzle: 170°C - 190°C</td>
</tr>
<tr>
<td>(example):</td>
<td>Zone 3: 160°C - 200°C</td>
</tr>
<tr>
<td></td>
<td>Zone 2: 150°C - 190°C</td>
</tr>
<tr>
<td></td>
<td>Zone 1: 140°C - 180°C</td>
</tr>
<tr>
<td></td>
<td>Feeder: 30°C - 60°C</td>
</tr>
</tbody>
</table>

Proganic Partners

Internationally renowned licensees are currently testing Proganic to produce Toys, household cleaning equipment, brushes (household and dental), gardening products, food packaging, storage and containers, water filtration systems and component parts to replace their existing plastic products. More interestingly, enquiries have been received from manufacturers of other materials including wood and ceramics who are seeking alternative natural products.

Future Plans

The Proganic dissolving leaf trademark offers a clear message to the consumer in reference to a 100% natural product and home compostability. Testing mechanisms ensure all Proganic products meet this criteria.

Currently Proganic has certain limitations in reference to temperature, at present it is not suitable for products in continuous use above 49°C, however research and development is addressing this issue without compromising the 100% natural ingredients and home compostability credentials.

Proganic products were launched at ‘Ambiente 2010’ Europe’s leading consumer fair and were very well received by trade buyers, consumers and the plastic manufacturing industry alike.

“Our aim is to establish Proganic clearly as the 100% natural alternative to conventional plastics,” says Oliver Schmid. The compound is currently under development to produce film, microfibers and blow moulded hollow articles.

Due to the initial success of Proganic Propper has now launched a separate company trading under the name PROGANIC GmbH. Interested parties should visit the website.

www.proganic.net
Fortune 500 company Newell Rubbermaid, whose portfolio of brands includes Rubbermaid®, Sharpie®, Graco®, Calphalon®, Irwin®, Lenox®, Levolor®, Paper Mate®, Dymo®, Waterman®, Parker®, Goody®, Technical Concepts™ and Aprica®, continually studies its consumers to design and deliver innovative solutions that also offer performance and value.

Through this research, Newell Rubbermaid’s Paper Mate division decided to produce a line of pens and mechanical pencils with biodegradable characteristics made with Mirel™ bioplastics (PHA) from Telles. Mirel is an innovative new material, a commercial bioplastic with a broad range of performance properties with broad applications in markets where non-biodegradable petroleum-based plastics are currently used, and is biodegradable in a wide range of disposal environments.

Lisa King, Vice President of Insights and Innovation for Newell Rubbermaid, said: “Paper Mate Biodegradable* products were developed as a direct result of consumer insights that showed a significant consumer desire for more environmentally conscious products offered at an affordable price.”

Considering the functional parts of mechanical pens and pencils, the product line was designed to have 60% biodegradable content. This meant that the barrel, nosecone, and clip would be made from Mirel P1003 injection molding grade. (Other Mirel commercial grades available include blown/cast film, thermoforming, and extruded sheet).

Once Paper Mate designed the writing set, traditional engineering techniques were applied to analyze the processing of the individual components, and then to design the commercial molds to make the pen components from Mirel P1003. Since these molds were being designed and built specifically for use with Mirel, the Telles technical support team was involved directly to make sure that the proper design recommendations were incorporated into the design.

Even the best designed and built molds will not function properly if the processing is not optimized. All polymers have an ideal processing window, and this is based on how well the material responds to the injection molding process. So, again, the Telles team was involved to make sure the processing was on target.

Some key processing parameters for Mirel P1003 include temperature profile, mold temperature, screw speed, screw back pressure, and injection speed. By balancing these parameters, Mirel can be injection molded efficiently and economically on existing equipment. Since the molds for the Paper Mate Biodegradable* products were designed with hot runners and thermal sprues, the amount of runner regrind was minimal, with all molds running with minimal scrap, at approximately 4%.

The converters Qingdao Changlong Stationery Co., Ltd. and Handmate Pen (Ningbo) Co., Ltd. have been operating the injection molds for Paper Mate Biodegradable* pens and mechanical pencils for several months with minimal issues. There continues to be improvements in the efficiency in the overall injection molding process. A reduction in cycle times has been achieved relative to traditional plastics.

This, combined with the lower processing temperatures, results in a significant reduction in energy consumption to produce the Paper Mate Biodegradable* pens and mechanical pencils from Mirel P1003 relative to conventional plastics. Measurements show a 20% reduction in electrical consumption in molding for the mechanical pencils as compared to ABS or polycarbonate. Modeling indicates a similar reduction in energy for the pens.

Advance demand is strong for Paper Mate’s Biodegradable* line, as consumers continue to express desire to be green through purchasing decisions.
Bill Mullenix, president of Everyday Writing with Newell Rubbermaid Office Products, explained: "While the cost of Mirel bioplastic is higher than traditional petroleum-based materials, consumers want green options and products like these are easy to market. We anticipate that increased sales volumes will more than make up for higher materials costs."

The Telles marketing team supported Paper Mate in the development of effective consumer education both on the packaging and through the product website. These efforts included instructions for proper disposal and a comprehensive set of FAQs on key industry terminology and certification standards.

This investment in consumer education is critical since the consumers making these buying decisions want to make a difference through their personal commitment to the environment and need to know their role. For instance, the pen components made of Mirel will biodegrade in soil or home compost in about a year, so consumers need to be aware of this and dispose of the components properly.

Bret Marschand, Senior Development Manager with Newell Rubbermaid Office Products, conducted a thorough evaluation of various biobased materials for use in their products. He selected Mirel for its unique combination of performance and biodegradability properties.

Mirel is a tough and durable material with heat and moisture resistance that rivals traditional plastics. For brand owners, Mirel can be molded in a range of colors, provides a high gloss finish, and the surface is suitable for printing and post-decorating.

Mirel bioplastics are biodegradable in home composting systems and industrial composting facilities, where these facilities are available. However, like nearly all bioplastics and organic matter, Mirel is not designed to biodegrade in conventional landfills. The rate and extent of Mirel's biodegradability will depend on the size and shape of the articles made from it.

As an example, Mirel cast sheet at a thickness of 28 mils (~0.71 mm), the type of material used to make retail gift cards, biodegraded in a home compost system in less than 3 months. Mirel P1003 meets U.S. ASTM D6400 and European EN13432 standards for compostable plastics, and is expected to be certified to Vinçotte OK Compost HOME for biodegradability in a home composting system.

"Mirel molds very well, processes in conventional injection molding equipment, and is durable in use. Add these performance characteristics to its biodegradability profile and we have found a remarkable material that fits into our global corporate sustainability goals," said Marschand.

The Paper Mate Biodegradable* pens and pencils are now available in the U.S., Canada, Australia, New Zealand, and Europe as the Mirel manufacturing facility in Clinton, Iowa ramps up production.

The use of biobased and biodegradable materials in product design allows both brand owners and their customers to participate in making environmentally-conscious buying decisions. Newell Rubbermaid’s Paper Mate Biodegradable* writing set is a real world example of how a global consumer retail brand owner experienced a successful new product launch by incorporating Mirel bioplastic into their corporate sustainability goals.

* Majority of the components are biodegradable in soil or home compost in about a year. See disassembly instructions on package.

www.mirelplastics.com
www.papernategreen.com
In today's lifestyle, the consumption of food and drink out of the home is increasing day by day and disposable tableware in fast-food restaurants, canteens, and popular events is now perceived as a necessity. This often poses problems in the management of waste: plastics tableware, which is disposed of with food scraps either in landfill or into incineration plants, and it is widely recognised that the disposal of organic waste in landfill is one of the major causes of greenhouse gas emission into the atmosphere.

The use of a full set of compostable tableware allows a huge amount of organic waste to be diverted from landfill and incineration plants. The tableware—compostable cups, plates, and cutlery—can be treated in industrial composting or in anaerobic digestion plants.

The cutlery plays a key role in promotion of an integrated system between bio-waste management and food service. A recent LCA study comparing different sets of disposables made of standard and compostable plastics, and different disposal options, showed that an integrated system adopting compostable cutlery and disposing of it in composting or anaerobic digestion offers significant environmental benefits in terms of CO₂ emission reduction and in terms of use of non-renewable energy.

Novamont has developed a specific grade that belongs to the second generation of Mater-Bi®, based on non-genetically modified crops and with a high content of renewable raw materials.

Mater-Bi meets the requirements of compostable utensils in compliance with FDA and European regulations for food contact. It is efficiently processed in injection moulding both with hot and cold runners, with cycle times as short as standard plastics.

What makes this grade the cutting edge in tableware is the possibility to achieve a good balance between in-use functionality, thanks to its stiffness and good heat resistance, and the compostability of the final product. That's why forks, spoons, and knives made of Mater-Bi are certified OK Compost according to EN13432 and BPI according to ASTM D6400.

Mater-Bi based cutlery with a full range of compostable items has been successfully introduced across Europe in school canteens, exhibition centres, sports events. GROM, the Italian ice cream producer recently introduced the compostable cups and spoons, together with shopping bags and bags for the recovery of the organic waste.

www.gromlovesworld.it
www.novamont.com
The Worlds First Bio Dispenser

The world’s leading trade fair for the cleaning industry, ISSA Interclean, saw for the first time a bioplastics entrant on April 26-29 in Amsterdam, as Italian producer QTS gave a sneak preview of its soon to be announced Ingeo™ (PLA) based bio dispenser product range.

QTS is an Italian producer of bathroom fixtures, with over 3 decades of experience in the design and styling of articles in plastic and metal for the professional cleaning market. Standing for Quality, Technology and Service, QTS has a wide product range mainly paper towel dispensers, soap dispensers, various other dispensers and bath accessories. Exporting worldwide, their products are used in communities, hotels, restaurants and offices.

At Interclean, QTS showcased their upcoming Simpla line, an Ingeo 3251 based injection molded range of dispensers for paper towel, liquid soap, and toilet tissue. Massimiliano Spinello, QTS Commercial & Marketing Director, explains the philosophy behind the ‘Simpla’ range and as QTS intends their new Ingeo based bio-dispenser family: "Simpla combines simplicity, design and eco values – products have been developed and designed combining form & functionality – creating a range that is a study of both design with the product’s origin (bio based material from plants)". Spinello describes the attributes of the Simpla line: brilliant transparency and gloss, resistance over time, temperature resistance equivalent to polypropylene, as well as a variety of end-of-life options which a bioplastic such as Ingeo is able to give.

Two tenets have been critical to QTS: that they will be able to competitively price the biobased product, and that the product eco-credentials stand up to tough scrutiny. According to QTS, they are attracted to the long term pricing stability they see for plant based alternatives to oil based materials, and for them, the relevant comparison from an environmental perspective is with ABS as the most used material which they are replacing. On this latter point, with QTS’ new bio-dispenser line, they note reductions in greenhouse gas emissions and non-renewable energy usage of 35% and 45% respectively, with Ingeo versus ABS.

In Amsterdam, QTS noted strong interest and response to the Simpla line, and will be commercially launching the product in June.

www.qtsitaly.it

Sigrid, this issue’s covergirl usually looks for function and design, when buying household utensils. but now I know, that it is also worth looking for the material, when I can do something good for our environment... "she says, after she learned about the Proganic watering can and other products.
The main area of application for bioplastics in previous years has been film extrusion. Recently the production of rigid parts via injection moulding has gained more and more importance among bioplastics applications. The main reason behind the production of non-durable films for packaging or mulching using bioplastics has been compostability. However, as a result of the rigid time frame if the product is to fulfil accepted standards (such as the European standard for the composting of polymers EN 13432 or the American ASTM D 6400) - only very thin sections will be acceptable. This is the reason why most films made from bioplastics fulfil the norms whereas most rigid parts fail.

The driving force behind making products from bioplastics is often the desire to meet the consumer’s demand for sustainable products. The most important argument is the content of renewable resource materials in the bioplastic. Another important aspect is the increased economic price independence of bioplastics’ from the price of crude oil.

Although composting is one disposal method, incineration is still a common waste disposal method used in Europe. Bioplastics made from renewable carbon release only the CO₂ which was originally absorbed into the plants from which the plastics were made. This CO₂ does not lead to an increase in the potentially dangerous greenhouse gas CO₂ in the atmosphere. Along with the previously mentioned points, a factor that makes incineration the most effective disposal route for bioplastics is the fact that the heat generated can be used for energy supply.

Bioplastics which are designed for the injection moulding process offer new and different options. These include a variation in the design as well as the possibility of producing technical parts. Another advantage, especially for the packaging industry, is to be able to offer a complete packaging concept containing both rigid parts and films to those customers that do not already use plastic packaging because of their philosophy of using only organic materials. Even consumer electronics benefit from the use of bioplastics (see fig.1 and page 42).

In contrast to blown film production, which uses existing machinery that has already proved to be effective, some reservations still exist in terms of the injection moulding of bioplastics. On the one hand this is based on existing knowledge of the complex process and its many steps, and on the other hand on unsuccessful trials with first generation bioplastics, some years ago, that may have created extra work. To convert
this negativity into interest and to create the desire to try the new bioplastics designed particularly for injection moulding it is essential to be able to benefit from the public interest in sustainable products and from the growth and success of bioplastics.

The most important requirement for successfully producing rigid parts from bioplastics is the compatibility of existing production equipment. Frankly, existing machinery and production tools that are designed for common plastics such as PP, PS or ABS are perfectly suitable for the processing of FKuR’s BIO-FLEX®, BIOGRADE® and FIBROLON® materials. However, a small investment may be necessary concerning the hot runner system and the clearances within existing tools.

One key to success is to reduce the residence time of the material. When compared with PS, for example, there are some bioplastics that can be processed with a reduction of 30% of the whole cycle time while others, such as PLA need longer cooling times due to the crystallisation process. While the mass temperature should not fall outside the defined temperature profile the processor should be informed, through recommended processing conditions, that the injection pressure and speed can be modified to fill the mould properly. The small processing window of bioplastics in terms of the temperature profile may result in the need for a new hot runner system. Commonly hot runner systems do not have a constant temperature along the whole length. This, along with the tendency of the materials to either freeze immediately or to burn if the temperature goes outside the processing window, can cause problems if improper hot runner systems are used.

After resolving the issues of the hot runner by applying a suitable system then the only thing that the machine operator needs is a bioplastic grade designed for injection moulding (pre-dried if necessary) as well as a little practice with the new materials. Some examples of successful products made from FKuR’s bioplastics in both multi and single cavity tools with hot and cold runners are consumer electronics, office equipment and catering articles.
When talking about PLA, and the World’s biggest production plant in Blair, Nebraska, USA, one usually thinks of NatureWorks’ two lines with a total annual capacity of 140,000 tonnes (~300 million pounds).

But I assume most people do not know, that this PLA plant is part of a huge Biorefinery Campus just outside this nice little town of Blair, Nebraska, about half an hour north of Omaha. And neither did I, before I visited the complex in late March of this year. I’m grateful to Steve Bray, Director of Manufacturing and Process Improvement and Steve Davies, Director of Communications & Public Affairs who welcomed me and showed me around.

The heart of the biorefinery, which is located directly on the banks of the Missouri river, is Cargill’s corn wet milling operation (After Cargill/Dow and Cargill/Teijin, NatureWorks today is a wholly owned subsidiary of Cargill). Multiple third party businesses operate on the Blair Biorefinery Campus in addition to Cargill’s corn oil, ethanol, erythritol, sugar, and lactic acid businesses. These include the NatureWorks LLC business, consisting of a their Ingeo PLA plant; Purac’s PGLA-1, another lactic acid plant for ‘non-PLA’ applications (Purac a partner of Cargill in PGLA-1); and Evonik, who operate their lysine facilities on the campus.

From corn to PLA and more …

But let me start at the beginning …

Nebraska, known as the ‘Cornhusker State’ is the third largest corn producing state in the USA. Climate, soil, irrigation (rain or water from local aquifers) and the farming techniques lead to a high quality, reliable and abundant supply of corn. In 2008 Nebraska produced about 1.4 billion bushels | 35 million tonnes of corn. The neighboring state of Iowa (US number 1 corn producer) contributed 2.2 billion bushels | 56 million tonnes. The Blair biorefinery gets its corn from a relatively
small area in its direct neighborhood of Nebraska and Iowa (more than 60% from less than 40 km or 25 miles). The farmers store their corn, which is being harvested from September to November, in silos on their own property and deliver it to Cargill year-round as it is needed.

Now, a kernel of corn does not only consist of starch, which is used for the production of PLA and other products. Besides the starch (~65%) it consists of ~23% cellulosic material (the hull and fiber). The germ makes up ~7% and the remaining ~5% are gluten (see picture).

The germ delivers about 85% of the corn-oil that can be used e.g. for cooking oil, margarine but also for printing inks, leather tanning and much more. The rest of the oil is found in the hull of the kernels, which is mostly used as animal feed. The gluten of the corn is protein rich and these proteins are exploited as animal feed but also for amino acids or fur cleaners. The largest fraction of useful components, the starch can be used for a huge variety of applications. For example 450,000 tonnes of starch are being used for corrugated paper in the USA alone every year. Other applications are adhesives, batteries, dyes or chewing gum. Dextrose from the starch, converted into fructose (HFCS= High Fructose Corn Syrup) by enzymes, is for example used for sweeteners. But the dextrose can also be fermented into bio-ethanol for fuels or into lactic acid for a variety of products. NatureWorks Ingeo PLA is an application that needs only a small fraction of this lactic acid. Assuming that about 19 pounds of PLA can be produced from one bushel of corn, you can easily calculate that the
Complete capacity of NatureWorks Ingeo plant would consume about 0.44% of the total corn production of Nebraska and Iowa (or 0.175% of the US corn production of 9 billion bushels).

If we now look at fig. 4, we understand the complexity of this biorefinery operation.

The sweeteners produced here can be found in a variety of consumer goods such as soft drinks, catsup, peanut butter and much more, even in shoe polish. Cargill produces bio-ethanol to provide renewable energy throughout the United States. More than 500,000 cattle enjoy SweetBran™ feed as a source of energy and nutrition. Another product of the campus are Cargill’s polyols. These corn derived, non-caloric sweeteners are used for beverages, food and pharmaceutical applications and as a bio-based component for the production of polyurethane (see bM 01/2008). The other companies on the biorefinery campus are Evonik and Purac. Evonik produces lysine, an essential amino acid, under the trade name Biolys®. Lysine is used for example to enhance growth and reduce waste in poultry and swine breeding. Purac operates in a joint venture with Cargill in PGLA-1. Here lactic acid is being produced for applications such as preservatives for food products, as mineral supplement in pharmaceuticals or cosmetics.

And finally NatureWorks LLC, which is the last company to join the campus (established in 1997), produces Ingeo PLA for wide variety of applications that can be found on store shelves around the globe. About 15% of the total dextrose of this biorefinery campus is being used by NatureWorks. The lactic acid, an aqueous solution, is pumped through pipes from the largest lactic acid plant in the world right into the reactors of NatureWorks where it is converted in to lactide ring molecules. Then finally the lactide is polymerized by ring-opening polymerization into Ingeo PLA. The rest of the story is well known to the readers of bioplastics MAGAZINE.

www.cargill.com
www.natureworksllc.com
What is Pland Paper®?

Pland Paper® is paper coated with 100% Ingeo™ (PLA, Poly Lactic Acid.) It is as water and oil proof as conventional treated paper. Pland Paper® can be processed into coffee cups, bowls, plates, lunch boxes, and so on. Pland Paper® is compliance with food contact packaging regulations around the globe and has been proven good biodegradation and compostability in accordance with ASTM D6868, DIN EN 15932 and ISO 17088 norms, also it has got several green mark certifications, which are approved by Biodegradable Plastic Institute (US BPI), Japan BioPlastics Association (JBPA, GreenPla), DIN CERTCO and VICTOTTE (OK compost). It is Natural, Safe, Eco-Friendly and Sustainable.
Continuously increasing crude oil prices, environmental responsiveness and new regulations on the use of non-renewable resources for both energy and materials have encouraged industry to research and develop more ecologically friendly bio-based composites. When considering modern ‘bio-composites’, with both a biogenic matrix (such as bio-based polyamides, see pp 50) and reinforcing natural fibres, great attention should be paid to their competitiveness with existing and well-optimised materials. To satisfy market expectations and achieve the required technical specifications some fundamental aspects must be challenged, for example processability, durability, competitive prices and similar, or improved mechanical performance compared to already-established materials. All these demands are the aim of the research presented in this article. The biobased polyamides used here were all supplied by Evonik in Germany. In 2008 Evonik Industries introduced its VESTAMID® Terra group of polyamides made from renewable resources. Besides the new bio-based polyphthalamide (PPA) Vestamid HTplus there are a PA 6.10 (Vestamid Terra HS), a PA 10.10 (Vestamid Terra DS) and a PA 10.12 (Vestamid Terra DD).

The logical way for bio-based composites

By using bio-polymers as a matrix, a natural and intuitive way is to reinforce them with biogenic fibres. Further advantages are significant weight and cost savings (most cellulose fibres are cheaper and much lighter than glass fibres - approx. 1.5 g/cm³ compared with 2.6 g/cm³). For this reason the relative properties of the bio-composites are often superior to those of glass fibre composites. In addition, natural fibres (NF) are combustible without residues while glass fibres are not. In consequence incineration with energy recovery is a favourable end-of-life option as an alternative to recycling. However, natural fibres also have disadvantages, for instance increased moisture absorption.

The properties of natural fibres are affected by many factors, such as variety, climate, harvest, maturity, degree of retting, etc. For this reason, only cellulose fibres of a technical quality should be used for composites. An additional problem concerning the reinforcement of polyamides with NF is the relatively high processing temperature, which is above 250°C, whereas the thermal degradation of NF often occurs above 200°C. Overcoming this drawback was the first step, within the framework of the research programme described here, towards optimising the PA NF composites. As a matter of fact, cellulose fibre can be processed completely with bio-based PA 6.10 and 10.10 and its petrochemical equivalents such as PA 6. The key is the method of processing combined with the tooling know-how and a knowledge of tailor-made cellulose fibres.
First results and further optimisation

As stated above, the correct choice of reinforcing fibres is of the highest importance, as the fibre parameters are a decisive factor in the overall composite performance. Therefore, the natural fibres used in this study are either man-made cellulose or ‘technical’ natural fibres (NF). Man-made cellulose is a chemical fibre of natural origin. The source of the fibre is cellulose pulp from different wood species. All tests were performed in both dry and conditioned states.

Figure 1 shows the tensile E-modulus of dry PA 6.10 composites. It is obvious that by reinforcing with cellulose fibres the stiffness increases significantly. Furthermore, the strength can also be noticeably enhanced, as is shown in fig. 2. However, the man-made cellulose fibre leads to considerably higher strengths compared to the strengths found in native natural fibre composites. Staple cellulose fibres exhibit much smaller diameters (approx. 12 μm) resulting in a higher aspect ratio leading to improved composite strength. Moreover, man-made cellulose fibres are thermally more stable than lignocellulosic fibres. As a result, thermally induced denaturation of the fibre structure is moved up to a higher temperature range. In consequence, the fibre is still able to transfer stress, ensuring improved mechanical performance of the composite, even if processed at temperatures above 250°C and provided that the processing method and tools are optimised.

A similar tendency can be observed when considering the impact test results (fig. 3). By reinforcing PA 6.10 with man-made cellulose, a significant enhancement by a factor 1.5 or 2.7 can be achieved using 15%-wt and 30%-wt of fibre.

On the other hand composites with NF show a lower impact resistance (fig. 3). This is a result of the overall mechanical performance of the fibre and its partial degradation caused by increased processing temperatures. Additionally, at 350 μm the diameter of NF is larger than that of man-made cellulose (12 μm), indicating a lower aspect ratio and decreased impact energy. Finally, natural fibres are characterised by lower strain-to-break than man-made cellulose, which is a further indicator for reduced impact strength in the composite. It is also of great importance that the test be performed in line with the instrumented procedure (EN ISO 179-2), which basically results in lower values compared to testing according to the analogue method (EN ISO 179-1). For that reason the values obtained are noticeably lower. Compared to PA 6.10 with 30% glass fibre (GF), where the impact strength is 10kJ/m², the impact resistance of bio-based composites was significantly improved.

Figure 1: Tensile E-modulus of dry PA 6.10 bio-composites with cellulose fibres.

Figure 2: Flexural strength of dry PA 6.10 bio-composites with cellulose fibres.

Figure 3: Charpy A-notch impact strength of dry PA 6.10 bio-composites.
The values represent excellent mechanical properties, especially taking into account the innovative bio-polyamide composites with man-made cellulose fibres. The levels achieved are close to those of petrochemical PA6 GF composites. The comparison is especially evident when looking at the composite density, which is noticeably lower for bio-based composites than for PA6 GF, indicating the enormous light-weighting potential of bio-composites (fig. 4).

It is typical for polyamides to absorb moisture. Increasing water content in the matrix decreases both the stiffness and the strength while at the same time increasing composite ductility and consequently its impact resistance. In general, natural fibre reinforced composites take up slightly more water than glass fibre composites, because of the hydrophilic nature of the cellulose and the fibre structure and composition (e.g. components such as hemicellulose, pectin, lignin etc.). However, PA 6.10 exhibits significantly lower moisture absorption compared to PA 6. Thus, its dimensional stability is improved. Figure 5 shows a comparison between PA 6.10 and 10.10 in both dry and conditioned states; composites were reinforced with 15% of NF and man-made cellulose fibres. It is obvious that increasing the water content influences the mechanical performance of the composite. Depending on the fibre origin, NF composites show lower moisture absorption than man-made cellulose reinforced PA. PA 6.10 is mainly processed at some 20°C higher melt temperatures than PA 10.10. In consequence, composites based on PA 10.10 are moulded by relatively gentle processing, achieving reduced fibre denaturation. This effect is evident when comparing the increased flexural strength of PA 10.10 NF composites (fig. 5).

Summary

The focal point of the investigation was on the processing ability and mechanical performance of bio-based polyamide composites reinforced with natural fibres. Within the framework of the study process optimisation with regard to process parameters and mould tools was evaluated. Bio-composites were processed on common production machines via compounding on a twin-screw extruder and subsequently injection moulded. A further focus was on the selection of cellulose fibres for reinforcement (without any additional modification).

Based on the know-how and long experience of the institute, combining high-temperature polymers with cellulose fibres was successfully realised. The range of mechanical properties of bio-composites is approaching the level of PA GF. Considering the low composite density, the relative properties are sometimes even better than PA GF, indicating a huge light-weighting potential.

The current activities of the institute are concentrated on improving the interfacial fibre/matrix adhesion. This will lead to significantly improved mechanical values and will also decrease the moisture up-take during the life cycle. Finally, the compounding process remains an area of investigation regarding improved processing, increased throughput and scaling up.

www.kutech-kassel.de
www.evonik.com
Composites Evolution Ltd, from Chesterfield, UK introduced a new family of materials, Biotex Commingled Flax/PLA and Biotex Flax yarns. The materials use a unique Twistless Technology to provide high levels of performance and processability normally associated with glass reinforced materials.

Although natural fibres are already being used to reinforce conventional plastics, for example in injection moulded or press moulded interior parts for the automotive industry, the natural fibres are generally short and randomly oriented giving relatively low mechanical properties. The Biotex materials are based on twistless yarns with long, aligned fibres to exploit the inherent mechanical properties of flax in load-bearing applications, with the added advantage of having a lower weight than conventional reinforcements such as glass fibres.

These fabric-based materials are believed to be the first of their kind, using long, aligned natural fibres to reinforce naturally derived plastics, and are said to provide a combination of sustainability, performance and processability not previously seen in composites.

**Sustainability**

Flax fibres are renewable and have a low environmental impact during processing. The matrix in commingled Biotex Flax/PLA is also derived from crops, giving a 100% renewable material that can also be recycled or composted at the end of its life.

**Performance**

Using Twistless Technology, the natural fibres in Biotex yarns are highly aligned to give up to 50% better fibre efficiency over conventional twisted yarns. The yarns are also easier to impregnate, giving improved fibre/matrix interaction and better performance.

**Processing**

The twistless fibres in Biotex yarns allow fast wet-out and impregnation. Biotex Flax/PLA commingled materials include an intimate blend of the reinforcement fibre and matrix polymer for easy processing by vacuum consolidation or press moulding.

Dr Brendon Weager, Technical Manager for Biotex, said “The development and use of renewable materials is becoming increasingly important in today’s environmentally conscious society. This new family of high-performance biomaterials is a major step towards harnessing the true potential of natural fibres and biopolymers, for the first time making high-performance biomaterials a reality.”

The product launch (at Composites Europe last fall) is based directly on the results of a project co-funded by the UK Technology Strategy Board’s Collaborative Research and Development programme, following an open competition. Besides Biotex Commingled Flax/PLA a version with Flax and PP is also available. MT

www.compositesevolution.com

Different weaves of commingled flax yarns / PLA fibers

Compression moulded plate of commingled flax / PLA

PLA fibre

Flax yarn
Biomaterial for Dragon Boat Decking

Dragon boats have existed for over 2,000 years, but it is only in the last twenty or so years that dragon boat racing has developed into a recognized international sport. In 1995 German company BuK GmbH developed a modern and measurable method of dragon boat building that laid the groundwork for turning the traditional Asian festival boat to a modern racing boat. Alongside modern materials such as glass-fibre reinforced unsaturated polyester (GUP), strict specifications require the use of natural materials to respect the boat’s Asian heritage. They explicitly stipulate that the deck planks and benches may not be made exclusively from plastic.

The roughly 12.5-metre long mahogany deck planks used up to now had to be hafted in the middle at least once to obtain the requisite length. Painstaking cutting and subsequent surface treatments potentially including several layers of varnish were necessary, making this the single most complicated component of a dragon boat.

The new deck plank is made from Hiendl NFC®, a natural fibre composite developed by H. Hiendl GmbH & Co. KG in Bogen, Bavaria. The material consists of 70% wood fibres and 30% polypropylene. Weighing only 0.66 kg/m due to its specially designed cavities, this natural-fibre-reinforced plastic profile lighter than traditional wooden ones. Profiles made from Hiendl NFC can be dyed in the mass during extrusion; the chosen colour and structure of the material makes it look like wood. The profiles are finished ready for use, i.e. no varnish or coating is needed.

It would be impossible to obtain such a wide range of wall thicknesses using pure, unreinforced polymers, as this would result in pockmarks and an uneven surface. The reinforcing material prevents shrinking, and the surfaces remain beautifully smooth.

The length, cross-section, colour and surface finish of the planks can all be made to order by extrusion, thus avoiding the need for joining, cutting and additional surface treatments. In addition, these innovative biomaterial planks are both more solid and also lighter than traditional wooden planks. They withstand paddle blows and moisture better. The annual maintenance work required up till now necessary after use is thereby reduced to practically zero.

With Hiendl NFC, BuK GmbH has produced a material that lives up to traditional values while also displaying all the modern characteristics that make the manufacturing process straightforward manufacturing and guarantee long, low-maintenance usage in even the most exacting conditions.

www.dragon.de
www.hiendl-kunststofftechnik.de
Packaging from nature, Packaging for nature

- Biodegradability with exceptional seal integrity
- Sustainable and high barrier
- Coloured and compostable
- Higher performances achieved when combined with other biopolymers
- Variety of ‘end-of-life’ options

use our imagination...

www.NatureFlex.com
Wood Composites for Toys

For more than 15 years the Institute for Natural Materials Technology (IFA-Tulln in Austria) has been working on wood composites (FASAL) to help establish a place for them in the injection moulding and profile extrusion markets. In a joint research project with the company FASAL WOOD KG, Vienna, Austria, lasting several years, new blends have been compounded and tested.

Depending on the customer requirement the wood composites Fasal could be

- based on renewables
- based on biodegradables
- based on conventional WPC materials

The easy-flowing type F337/31 in particular has been able to convince some toy makers of its extraordinary possibilities in design and function. Fasal's general manager Ing. Kresimir Hagljan works closely with his customers right from the preparation of product drawings through tool making to manufacture of finished parts.

Toys

"Babel Pico", a strategy game for two people, was presented by Swiss company Cuboro AG at the International Toy Fair 2007 in Nuremberg, Germany.

The 30 mm cubes are produced using interchangeable sliding parts and hot runner. Despite the significant volume of the parts no shrinkage occurs. The surface has a soft feel. "We wanted a solid, large cube with a relatively complex shape," says Matthias Etter, Project Manager for the strategy game. "The injection moulding technology seemed suitable, but all materials tested had some drawbacks, be it technical, cost-related or ecological. The wood-injection-moulding material comprises different advantages."
A new game of skill from Ravensburger called ‘Kipp Kipp Ahoi! (see photo left) uses Fasal material in an application that could not be economically accomplished using conventional materials based on renewables such as cardboard and solid wood. The screws are produced in the appropriate colours using an 8-cavity tool. The body of the ship combines the mating components for the screws with a stable mounting for the printed cardboard element.

Musical instruments

A special instance of resource conservation was introduced by Herbert Neureiter in the Austrian Tyrol. Clarinets, which are often made from endangered African Blackwood (ABW), can be produced by injection moulding using Fasal material. The risk of splitting and the absorption of moisture are virtually nil. “In spite of the lower weight of about 10% the material shows a very good sound behaviour and there are hardly any differences to massive wood,” says Herbert Neureiter. Customers are given a 5-year warranty for dimensional stability. The high density of the Fasal material results in similar sound characteristics to those of solid wood.

Furniture

The direct moulding of internal and external screw threads represents an interesting possibility for the furniture industry. Overmoulding of metal threads is also a possibility. Both options have already been used for toys and kid’s furniture by ‘HABA - the children’s inventor’. “The synthesis of a technical requirement in combination with materials from renewable resources is interesting for us,” says Matthias Löhnert, Quality Management at Habermaß. An additional advantage of this Fasal material is its surface feel, which is very close to natural wood.” Also some other Fasal connecting elements are fixed using PVA adhesive.

Biodegradable matrices

Because of the continuous development of the bioplastics market a redevelopment of the Fasal compound was an obvious step. At the IFA in Tulln studies and projects for the industry, focussing on renewables and biodegradables, are routine. So a new, upgraded compound, FASAL BIO 322/14, was on the market after a very few months. Compared to conventional Fasal the new injection moulding material based on renewable and biodegradable raw materials features a high degree of flexibility and impact strength. Thus resilient parts can be produced, such as those required by the toy industry.

This new material is the first result of the ‘Wood COMET’ research project. As well as testing the compatibility of wood and natural fibres in combination with bioplastics, various ‘bio-additives’ are tested. Requests from manufacturing companies show the high level of demand for bioplastics, but prices and process parameters have to be optimised for successful market introduction.

www.ifa-tulln.ac.at
www.fasal.at
Natural Fibres

NF Bioplastics

widely used in many industries, plastics have become the source of white pollution. While the world is struggling to deal with this problem, GreenGran has been ardently advocating a new technology that replaces glass fibres with natural materials. Natural fibre reinforced polymers, with qualities that rival engineering plastics, are paving a new path to a better environment.

In the 1990s European countries began to focus on recovering, reusing and recycling automobile materials and spare parts, especially glass-fibre reinforced plastic parts which are widely used but difficult to recycle. With financial support from the UN and EU, the Wageningen University of the Netherlands commenced research on the development of natural fibre reinforced polymers. The result was the invention of the technology to produce natural fibre reinforced plastic granules that became a registered patent in the late 1990s. A few years later GreenGran was founded as a spin-off company, aiming at production, marketing and sales of natural fibre reinforced (bio)plastic granules for injection moulding applications.

Using sustainable and renewable natural plant fibres [such as flax, jute, hemp and kenaf] and through industrial production techniques that blend them into plastics, GreenGran’s granules are made from the combination of these natural fibres with polypropylene, thus reducing the use of petroleum products. Also, there were other ideas being tested with the aim of overcoming problems in the production of natural fibre reinforced plastics suitable for injection moulding, such as feeding the natural fibres into the pelletization process and maintaining high technical properties throughout the pelletization process. In GreenGran’s case the development eventually resulted in a material that exceeds the technical properties of previous natural fibre reinforced granules and reaches properties comparable to glass fibre reinforced plastics (see table and graph).

<table>
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<th>Property</th>
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<tr>
<td>Tensile Strength</td>
<td>60.4 MPa</td>
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<td>Charpy impact notched</td>
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<td>Vicat softening point</td>
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<tr>
<td>Density</td>
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</table>

(all photos: Philipp Thielen)

Article contributed by
Martin Snijder, CEO
GreenGran b.v., Wageningen, The Netherlands
to Save Coral Reefs

Five times stiffer and 2.5 times stronger than polypropylene, it will not cause wear and tear to the screw and the mould as glass fibres do, and unlike glass fibres, it does not pose safety or health risks. Its recoverable component comes from these natural plants and can occupy over half of its weight (up to 80%). All of these features make it suitable for the production of durable products.

The many advantages of these granules include good insulation, dimensional stability at high temperatures, high thermal deformation temperature, flame retardant, impermeability, possessing a stiffness and strength similar to traditional glass fibre filled polypropylene, can withstand long machine resistance time, low water absorption rate, high resistance to UV radiation and demonstrates normal flow behaviour, making it the best substitute for glass-reinforced plastic.

For a material to be genuinely environmentally friendly, its entire production process should be a closed system. The waste released by each production process should be usable in the next process, forming a cradle-to-cradle production cycle. In addition, as the raw materials of GreenGran’s natural plastic come from plants and petrochemicals, the whole product can be collected and reused.

Laboratory figures showed that GreenGran natural fibre reinforced polymer products can be reused as many as seven times. Even when the product has reached the end of its life cycle, it can be collected and made into energy pellets for electricity generation, during which only water and carbon dioxide will be released when combusted.

To promote its granules, last year GreenGran moved from innovation to commercialization. It shared its technology and partnered with Bio-Natural Technology Co., Ltd. to form GreenGran BN (HK) Limited in Hong Kong, from where its industrial production was established. The granules are currently produced for a range of applications in automobiles, construction materials, packaging, toys and electronic products.

Custom-made orders are also available to cater for clients’ products. The type and amount of natural fibres can be adjusted to manufacture products of different features and appearances. These include UL94 FR V0, V1and V2 grades.

Apart from conventional industrial uses, GreenGran is initiating research to apply its bio-based materials in innovative applications. Among them is a partnership with Anome where, in co-operation with Dutch Waterworks (ITC), Havenbedrijf Rotterdam and Boskalis, 35,000 protective blocks made from GreenGran granules were placed on riverbanks and dams to prevent riverbank erosion. Experiments have shown great results.

One of GreenGran’s major fields of interest is the substitution of the matrix material with bioplastics while maintaining good technical properties. GreenGran already offers a variety of granules made from natural fibre reinforced PLA and has just released one grade using PHB from Tianjin’s production facility in China (see bM 02/2010, p. 28/29) that was inaugurated last year.

Those materials will decompose in a specified time period during which no harmful substances will be released, making it ideal for different areas of application.

Coral reefs around the world are dying in massive numbers due to various causes. The traditional method of reviving the coral colony is by sinking a ship that acts as a new home for corals. But the ship’s paint and other substances will pollute the sea. Better, GreenGran natural fibre reinforced bio-polymers will slowly disappear and be replaced by coral reefs. This meets the purpose of coral reef rebuilding.

“We care a lot – care for the environment, care for our clients’ economic return, care for your products/market combinations and care for a sustainable supply chain. GreenGran is solution- and service driven, aiming at working with you to co-create the transition from the oil-based economy to the bio-based economy.”

www.greengran.com
From a historic point of view, for more than 2,000 years hemp has been an important raw material for industry. Hemp fibres were used for the manufacture of technical products such as ropes, hawsers and boat canvas, as well as clothing textiles and paper. In the 1990s, hemp was rediscovered throughout the world as an important raw material for bio-based products in a sustainable bio-economy and ever since then has been in high demand. The most important cultivation and manufacturing regions are Europe and China, and the most important applications are bio-based composites (natural fibre reinforced plastics) as well as construction and insulation materials. The bio-based materials sector in particular still has large, untapped market potentials for both the reinforcement of mineral oil based plastics and, to an increasing degree, for bio-based plastics.

Hemp - A Sustainable Raw Material for Bio-based Composites

Success story in the automotive industry: Current trends and new applications

In the year 2005 (more recent data is not available) in the EU about 40,000 - 50,000 tonnes of natural fibre composites (wood not included) were used in the automotive industry, requiring 30,000 tonnes of natural fibre. European flax (about 65%) and hemp (about 10%) were used, with the remaining 25% covered by imports from Asia (jute, kenaf, coir, abaca). Natural fibre compression moulding is the dominant processing technique (share of > 95%). It is an established and proven technique for the production of extensive, lightweight and high-class interior parts in medium and luxury class cars. Advantages are a lightweight construction, its crash behaviour, deformation resistance, lamination ability, and also, depending on the overall concept, price. The disadvantages are limited shape and design forming, off-cuts, and cost disadvantages in the case of high part integration in construction parts. These advantages and disadvantages are well known. Process optimisation is in progress in order to reduce certain problem areas such as offcuts and to recycle wastage. By means of new one-shot compression moulding presses. Soft surfaces can also be directly integrated, something that has not been possible so far with injection moulding.
Between 2005 and 2009, the use of natural fibres in the European automotive industry did not expand, and in Germany even slightly decreased, after it had grown in double-digit figures each year between 2000 and 2005. Since 2009, however, there has once again been an increase in demand: new models from almost all automotive companies that will be released on the market this or next year do have considerably more interior parts made once again with natural fibre reinforcement. On the one hand this is due to the highly advanced development of the materials and the fact they have proven themselves in practice. On the other hand, however, it is also due to the increasing interest by the automotive industry in bio-based materials and lightweight construction – in both fields natural fibre construction parts can score. In addition, further cost and weight reductions were achieved in recent years, especially with regard to compression moulding.

Furthermore new trends are becoming apparent: the automotive manufacturers not only want to use bio-based materials, but also want to show them to their customers. While until now natural fibre construction parts have disappeared under a lamination, thus becoming invisible to the customer, in the near future vehicles will be launched that exhibit the natural fibres under transparent films or lacquers, showing completely new surface effects. Another trend can be noticed in the development of making the plastics matrix bio-based as well, i.e. producing interior parts from PLA or bio-based PP and natural fibres. While such 100% bio-based compounds will soon be found in Japanese cars, in Europe this will still take a while. With demand increasing again, plus new concepts and the support of bio-based products by politics, sales of 40,000 to 50,000 tonnes of natural fibres could be achieved in Europe by 2015, at least 10-20% of which could be covered by European hemp.

Other applications

Apart from the automotive and construction industry, there are numerous applications with a smaller volume such as briefcases, other types of cases, various consumer goods (e.g. letter scales, battery chargers, toys) or trays of grinding/sanding discs and cremation urns. The latter represents a good example of a 100% bio-based product: The urns are produced from PLA, reinforced by hemp fibres, and are fully biodegradable.

As well as the examples mentioned, and in addition to the aforementioned compression moulding, injection moulding plays an important role. The increasing availability of high-grade natural fibre injection moulding granulates will help to quickly develop new applications here.

**Price indices for natural fibres, crude oil and polypropylene (per Euro basis)**

*Sources: nova-Institut 2010, www.kiweb.de, FAO 2010*
New processing techniques

For some decades, in the EU and North America, there has been intense research going on into new processing techniques for flax and hemp fibres, in order to make the development of new, high price fields of application possible for natural fibres. There are two outstanding processing techniques that are close to commercial implementation, and today already producing modified hemp fibres amounting to several hundred tonnes per year. First is the Crailar Process from Canada, which focuses on the use of hemp fibres in the textile industry and for special bio-composites, and second is the ultrasonic processing technique of the Ecco Group Company from Germany which focuses on high-grade technical fibres.

Availability and price development of natural fibres – A chance for European hemp?

While the technical natural fibre market is increasing worldwide, the question of prices and security of supply arises. In important cultivating countries in Asia, the cropping areas for jute and kenaf cannot be extended because there is considerable competition for areas to be used for other purposes. The situation is better regarding sisal: here an extension of cropping areas is possible in the dry regions of Africa and South America – places, where hardly any other crop can be cultivated. But European production is also under pressure: the areas used for flax are decreasing due to strong competition from areas enjoying subsidised bio-energy production, as well as the dependency on exports to China where less textile long flax fibres are now being demanded. As for hemp, an extension of cropping areas is possible however, provided that rates of return similar to those of the food and feed sector and energy crops can be achieved. Areas under hemp cultivation are also on the rise in China, with hemp being expected to replace cotton in the clothing textile sector.

In December 2009, Bangladesh imposed a ban on jute fibre exports for the first time and it was not before February 2010 that it was partly suspended for certain qualities. The reasons for the embargo were to be found in three years of poor harvests and increasing demand particularly from India (packaging) and China (composites), threatening a shortage of the necessary raw material from the Bangladesh jute industry. Due to the embargo, jute prices rose by 50 to 100%. At the same time sisal prices were increasing, too, due to a severe drought in East Africa.

80% of jute and kenaf are used in Asian packaging (bags), sisal particularly in the form of tows and harvest belts. In contrast to these, natural fibre composites still constitute small markets that can be supplied quite easily.

As a result of farmers reacting more quickly to changes in demand, rates of return and a local shortage of area, there has been a general trend leading towards a more dynamic agricultural market with more volatile prices, and this, fueled by speculators, is now affecting the world of natural fibres. For a long time, prices have been quite stable compared to other agricultural products or mineral oil but it is expected in the future that natural fibre prices will definitely stay below 1 €/kg so that they remain attractive for composites.

The graph shows the price development of important natural fibres, and as a comparison, the price development of mineral oil and polypropylene. European flax and hemp short fibres, after a long period of price stability have only recently shown moderate price increases, and are currently showing particularly good price stability - a price rise of less than 10% in over seven years.

To sum up: exciting times for European hemp which, with adequate framework conditions, has considerable growth potential.

www.eiha.org
executive office: www.nova-institut.de
Value creation in consonance with economy, ecology and social responsibility, this was the vision that drove BIOWERT Industrie GmbH in Brensbach, Germany (the company name could be translated as ‘bio-value’). In the Odenwald area, south of Frankfurt/Main, Biowert built the World’s first production plant of this kind, geared to the principles of a truly ‘green’ bio-refinery. This special plant produces economically environmentally friendly products of high quality based on a raw material that is abundantly available in the area - grass.

“The utilisation of meadow grass opens up new and safe potential for added value for the local farmers,” says Dr. Michael Gass, founding member and CEO of Biowert. The combination of the high absorption of CO₂ by the grass, the large extent of CO₂ neutrality of the production process, the unique concept of re-utilisation of the process water as well as the use of waste heat coupled with a biogas-unit, means that an industrial process without environmental burden becomes possible.

The principal is basically simple: In the grass processing plant cleaned grass is mechanically broken down into its constituents with the help of hot water coming from the biogas unit. The defibred cellulose is separated from the liquid fraction using specially developed presses. Over several steps the process delivers cellulose of a very high purity.

The residual components of the grass plant remain in the process water. This ‘grass slurry’ is led directly into the biogas unit, where it is converted into biogas and subsequently into electricity and heat. The residual process water from the bio-gasification process is sent back to the grass processing plant.

The heat needed for the process water and for the fibre drying comes from the biogas unit. The common energy system of both units makes it possible to completely use all of the heat generated in the process.

In addition the residue of the biogas unit is separated into solid and liquid fractions which are sold as solid and liquid fertilizers [brand name AgriFer®]. The biogas itself is converted into electricity and heat by two block heater/power plants [gas driven generators at 716 kW each]. The biogas unit not only uses the biomass from the grass processing unit [one third of the total raw material input] but also one third each from food processing company waste and cattle-slurry from neighbouring farmers, a total of 45,000 tonnes of organic input per annum. Thus the unit can produce 11,000 MWh of electric power per year.

The dried grass fibres however [and this is why we report about the installation in bioplastics MAGAZINE] are used as an industrial raw material for insulating purposes (AgriCell®) and as a filler for PP, PE or even Mater-Bi® [Agriplast®]. 50%, and up to 75% %, by weight can be added to the matrix thermoplastics. The compounds can be injection moulded and extruded. Potential fields of application are consumer goods and particularly the construction sector.

The main advantages are:
- easy availability of cellulose fibres from renewable grass
- gentle production of the granules on pellet-presses or palltruder®
- high fibre content: 50-75%
- medium mechanical properties
- easy flow - normal cycle times
- favourable price
- sustainable production process
- design ‘close to nature’
- residue-free incineration
- lightweight applications
American Leistritz Extruder Corporation has installed ZSE-27 and ZSE-50 MAXX twin screw extrusion systems and related auxiliary equipment in its’ New Jersey process laboratory to process ‘wet’ PLA (and PET) on a twin screw extruder in combination with direct sheet extrusion. PLA is typically dried before being processed on a single screw extruder to avoid hydrolysis/degradation. Undried PLA, pellets or regrind, is metered into a co-rotating twin screw extruder that is equipped with multi-stage vacuum venting to minimize and avoid hydrolysis. A gear pump, screen changer and flexible lip sheeting die are attached to the twin screw extruder prior to a 3-roll stack that cools and forms the PLA sheet. The result is a quality product with dramatically less energy consumption.

PLA processes are heat and shear sensitive, as well as torque intensive. The Leistritz ZSE-MAXX series is particularly suited for this application due to increased torque capabilities combined with a higher 1.66 OD/ID ratio as compared to competitive twin screw extruders. The ZSE-MAXX series also integrates an improved barrels cooling design for increased heat transfer capabilities, which is particularly beneficial for PET processes.

The following equipment is currently available for PLA demonstrations/development trials:
- ZSE-27 and ZSE-50 MAXX model twin screw extruders
- Loss-in-weight feeders for pellets, regrind, powders and liquids
- Screen changers and gear pumps
- Sheet dies from 10” to 40” width
- Water-ring, oil ring and rotary-vane vacuum pumps
- 3-roll stacks, 14” wide and 42” wide

In addition to the equipment denoted above, a wide variety of additional auxiliary equipment is available to support a range of processes, including desiccant dryers, coextrusion tooling, a supercritical injection unit, strand and underwater pelletizing systems.

www.leistritz-extrusion.com
New BoPLA Film

Taghleef Industries, (Ti) one of the largest manufacturers of BoPP (bi-axially oriented polypropylene) packaging films in the world, is launching a new bioplastics packaging material.

Throughout previous years Taghleef Industries, headquartered in Dubai, United Arab Emirates, has continuously grown by size as well as by the product offering to the market. In 2008 Radici Film, Italy became part of the Group. Realizing the growing demand for more sustainable packaging solutions, Ti has invested into this new film technology and will start its production in their Italian plant near Venice later this year. Ti acknowledges that Bioplastics have emerged as real alternatives to oil-based plastics in Europe, USA and Asia and major market players are investing. “We have established a market position as a reliable, long-term committed supplier to the industry. We believe that this continuity and stability will support the market growth for our new BoPLA films. The market response so far is highly encouraging.” comments Valerio Garzitto, CEO of Ti Europe.

Frank Ernst, Product Manager and experienced in the Bioplastics market explains: “Our new BoPLA film range is based on the PLA [Poly Lactic Acid] resin Ingeo™ from NatureWorks. These resins are based on 100% renewable resources and are registered by AIB Vincotte under the OK Biobased certification scheme with the highest 4 star rating of renewable carbon content. Recent developments in the market left a gap which we are delighted to fill guaranteeing the continuous supply of BoPLA films to our customers. The market response on Ti’s move is very positive and customers will benefit from our vast experience as a reliable supplier to the flexible packaging industry.”

The product’s properties allow it to be used across most food packaging sectors, including perishables, as well as for lids, and non-food applications too.

Ti is currently undertaking film testing processes to ensure the new production process meets its exacting standards, and that the new product meets the quality expectations of Ti’s exacting customer base.

The new portfolio will comprise a transparent film and a metallised version. It has outstanding optical properties (high gloss, low hazel, superior mechanical strength [tear resistance], strong seals at low temperatures, excellent twist and dead fold, and high moisture transmission. It is made from an annual renewable source, so is truly sustainable; is biodegradable under composting conditions, and is oil and fat resistant.

“The future will bring a wide array of new applications and developments. We are prepared for this and are looking forward to helping create the next generation of packaging materials,” concluded the product manager Frank Ernst.

www.ti-films.com
Cellulose Based Bio-Keyboard

Fujitsu recently introduced the World’s first injection moulded keyboard made from renewable materials. This newly developed eco-keyboard ‘KBPC PX ECO’ has been launched under the label ‘Green IT’. For some of the component parts Biograde® cellulose ester compound from German supplier FKuR is being used.

This new Eco-Keyboard underlines Fujitsu’s Green IT commitment to saving CO2 emissions, and represents a further innovation for Green IT. “In order to reduce the dependency on oil, Fujitsu’s new keyboard replaces 45 percent of plastic components with materials from renewable resources”, confirms Jürgen Geiger, project manager in charge at Fujitsu Technology Solutions.

For the keyboard base, Biograde C 7500 CL from FKuR has been chosen. “The ease of processing using existing production equipment and the excellent mechanical properties of Biograde were the decisive factors for choosing this material from FKuR”, says Thomas Raab, responsible project manager at Amper Plastik, a high-quality, technically superior plastic product and injection moulding producer with 50 years of experience. “Parts made from Biograde meet the special requirements for keyboards and in some cases even exceed the properties of oil-based plastics,” as Mr. Raab added.

PLA Drawing Instruments

In response to the increasing demand for environmentally responsible products as well as their own mission of acting as a responsible company, Linex, of Taastrup in Denmark, introduced an innovative series of school and office drawing instruments made from 100% natural corn starch based PLA. Each instrument is printed with biodegradable ink and packed in cardboard packaging made from recycled board and printed with biodegradable, vegetable ink. The products and the packaging are biodegradable and can be disposed of as domestic trash.

“Environmental responsibility is with us, and the time has come to include environmentally-friendly rulers,” as Lisa Mikkelsen of Linex points out. “Now our rulers have become really ‘green’”. Making plastic from maize starch helps reduce CO2 emissions. Maize absorbs CO2 as it grows and therefore has a beneficial effect on the natural cycle. The production of the granular plastic pellets and the drawing instruments produced requires substantially less energy, which is very positive. When disposing of plastic products made of maize, the material may be granulated and composted, and will not have a negative impact on the environment

A special version of the set-square was produced for the German mail order company memo AG of Greussenheim, a company that supplies environmentally friendly office equipment.

Claudia Silber, PR Manager at memo says: “Our carefully selected and tested product range makes it easier for the consumer to buy ecologically sound and socially acceptable alternatives. Value for money is also a key factor here: it is only where socially and environmentally acceptable products are available at a market related price that we will succeed in achieving significant market penetration, and with it a meaningful contribution to the environment”. **MT**
PLA Interior Signage

An innovative new interior signage system was recently exhibited at NatureWorks’ Innovation Takes Root conference in Dallas, Texas. Accent Signage Systems of Minneapolis, Minnesota, USA use Ingeo™ PLA for sheet materials and injection molded frames for the fabrication of their Intaglio™ Signage System. This system is fully ADA (Americans with Disability Act) compliant and features tactile letters and graphics as well as Accent’s patented Raster™ Braille system and was developed specifically for LEED® (Leadership in Energy and Environmental Design) green building applications.

It is perhaps the first complete interior signage system in the world to be produced from a renewable plant resource. We have been working on characterizing materials suitable for the custom interior signage systems for about 18 months now, explained Dr. John Souter, Director of Operations for Accent Signage Systems and having NatureWorks located close by has allowed for the technical cooperation necessary to successfully bringing this unique signage system to market in a short period of time. Controlling the surface tension as well as tensile modulus and glass transition temperature are all critical attributes when developing materials that can be digitally imaged, CNC routed and LASER cut efficiently, without causing any physical or visual degradation in the finished appearance of the signage.

www.accentsignage.com

PLA-based Paper for Laser Printing

Scientists from the Montanuniversität in Leoben, Austria, recently developed reprographic paper completely based on biopolymers. It not only looks and performs like normal paper, but it also claims to be water-resistant and to have certain ecological advantages.

Prof. Dr. Stefan Laske from the Institut für Kunststoffverarbeitung (Institute of Plastics Processing) in Leoben points out that regular paper needs raw materials such as wood and water, which are not equally available in every region. As a consequence of the earthquake in Chile the European pulp industry suffered a shortage of pulp and had to reduce its production. Laske points out that synthetic paper based on renewable polymer resources might be an alternative if it meets the high demands of modern printing processes and normal use - for instance paper for laser printing must be stable at temperature peaks of up to 180 – 200°C. Furthermore synthetic paper must exhibit ecological and economical advantages such as a low environmental impact or low investment. In cooperation with the Polymer Competence Center in Leoben (PCCL) Laske developed a process to produce synthetic paper based on renewable raw materials - a process that could quickly be adopted on an industrial scale using existing technologies.

The new paper is made up of three layers. Two highly filled outer layers meet the tactile, visual, thermal and mechanical demands, whereas a foamed intermediate layer reduces weight and therefore the costs. Laske says that the most difficult aspect when using PLA for printing with laser technologies is the temperature peak up to 200° in the fuser unit. To prevent premature melting of the PLA matrix the cover layers were crosslinked by high-energy radiation. This hinders crystallization and the material exhibits an amorphous character.

Printing tests with a conventional laser printer produced faultless results. The printer used handles paper at a speed of about 50 mm/s and reaches around 190°C in the fusing unit. Lasker says that he alternately printed one synthetic sheet and one reference sheet for comparison purposes. With regard to the print quality no significant difference was visible. He even found that the adhesion of the toner was better on synthetic paper.

The new product was analysed according to the ISO 14044 life cycle assessment and the life cycles of the regular and the synthetic paper were compared. The results show that the synthetic paper has ecological advantages if recycling is included. Laske says that the advantages are even more significant if factors are taken into account that favour the new product, e.g. CO₂ retention by the cornfield or production of PLA from secondary plant products. BSL

www.unileoben.ac.at
Application News

Correction Roller
Shells Based on PLA

ECOfort is the latest Correction Roller from the Pritt stationery range by Henkel AG & Co. KGaA, Düsseldorf, Germany. The newly developed and innovative natural ‘Arctic’ material sets new standards as it replaces a high technical performance plastic with a sustainable renewable material. The Pritt correction roller won the 3rd prize at the Bio-based Material of the Year 2010 awards (see p. 6).

The ECOfort correction roller allows quick, clean and accurate corrections on paper. Due to its premium correction layer the corrected area can be written over instantly. In addition to a perfect correction result and functionality aspects the roller design focuses on aesthetics and ergonomics. The artic white colour of the device emphasises the correction pureness with the green print reflecting the natural plastics of the shells. The solid feel and tactile sensuality endorses the high quality of the Pritt brand.

Pritt ECOfort is the first correction roller in the world made of renewable resources to be launched on the market in 2010. The development lasted over 12 months in which the base PLA material was optimised to increase specific technical values in line with standard plastics. In parallel the processing and manufacturability of the material was improved.

Extensive laboratory research was followed up by technical testing. Melt flow, colour stabilisation and heat resistance were constantly challenged and improved with every test run. Functional testing, accelerated time/temperature simulation and drop tests pushed the material to high performance, every small step resulting in improved solutions.

Both compounding and Injection methods were tweaked in order to advance and perfect the processability. Machines were modified and changed in small measures to increase performance and output.

The new Pritt ECOfort is the first correction roller in the world made from approx. 89% natural plastic [used for the device shells] resulting in significantly reduced CO₂ emissions comparable to planting 1,000 new trees.

The Pritt development team continues to push for further enhancements to the new ‘Arctic’ material and further innovative and exciting applications in the stationery sector are expected. MT

www.henkel.com

Competition for Famous Coffee Capsules

This year a Swiss company is attempting to break the monopoly position enjoyed by Nespresso. The Ethical Coffee Company SA, located in Fribourg and founded by no less than the former Nespresso boss Jean-Paul Gaillard, has developed a capsule that can be used with the usual Nespresso machines – something that hasn’t been done before. According to the French paper ‘Le Figaro’ the French supermarket chain Casino will start in May selling an alternative that costs 20% less and claims to offer the same taste. Soon the alternative capsule might be sold in different supermarket chains worldwide and therefore could be able to crack an outstanding sales system that is based on exclusive selling points run by Nespresso itself.

The capsule technique is protected by several patents and Gaillard says that he has found a gap in the patents that allows him to produce a competitive product. Gaillard is sure that his new product not only gives the customers a choice but also improves the ecological balance. In contrast to the aluminium, which Nespresso uses, Gaillard decided on a capsule made from biodegradable plant fibres that degrade in only a few weeks. It is true that aluminium capsules are collected for recycling but in many countries consumers are much less conscientious about collecting them, say the Swiss. The ecological aspect therefore could turn out to be a major selling argument for the Ethical Coffee Company. Aluminum capsules must be collected for recycling or need to be disposed of separately and furthermore they exhibit an inferior CO₂ balance. BSL
Bio-based Resin for New Boat Construction

Canada’s largest fiberglass boat builder, Campion Marine Inc., (Kelowna, British Columbia), is bringing improved environmental performance to its customers by being the first boat builder in the world to manufacture all of its boats with Envirez® bio-derived resin from Ashland Performance Materials. Envirez resin is the first resin that uses a substantial amount of soybean oil and corn derived ethanol in its formulation.

“Ashland’s bio-based resin delivers the performance characteristics we want for our boats and it reduces our reliance on petroleum-based counterparts,” said Brock Elliott, general manager, Campion Marine. “We are putting Envirez resin in all our boats. It is the right next step, and it is right for our world. Envirez resin’s performance delivers higher ratings for strength and elongation. Our vision is to build the best from the best and that makes Envirez resin a natural choice.”

Ashland selected Campion Marine to test Envirez resin in 2008 resulting in the world’s first bio-based resin boats being built. Data from those tests support Envirez resin’s use in high performance and recreational watercraft. Based on confirmed research, the move to Envirez resin by Campion will eliminate more than 45 tonnes of CO₂ from entering the atmosphere.

“We are pleased to be working with a great company like Campion to bring this technology to the boating public,” said Mike Wallenhorst, director of product management, Ashland Performance Materials. “Envirez is a fantastic product that offers outstanding toughness and is a big step towards a totally renewable resin. It’s exciting to realize that hundreds of boats made from Envirez resin will soon be navigating the world’s waterways thanks to Campion.”

Campion Marine has been building high-performance sport boats and cruisers for 36 years. The company builds the Allante line of sport boats and cruisers, the Explorer sport utility watercraft, Chase high-performance boats and the Svfara wake/surf tow boats. They manufacture more than 37 models and 48 variations of boats ranging from 4 to 9 meters in length and market and sell their boats in more than 30 countries.

Ashland Performance Materials is the global leader in unsaturated polyester resins and vinyl ester resins. In addition, it provides customers with leading technologies in gelcoats, pressure-sensitive and structural adhesives, and metal casting consumables and design services. MT

www.ashland.com
www.campionboats.com
This new book is available now. It is written in German, an English version is in preparation and coming soon. An e-book is included in the package. (Mehr deutschsprachige Info unter www.bioplasticsmagazine.de/buecher).

The book looks at the relationship between man and nature and highlights the key sustainability initiatives of the chemical industry. The eco-efficiency analysis is described as a management tool incorporating economic and environmental aspects for the comprehensive evaluation of products over their entire life-cycle. Another chapter describes a holistic approach to define sustainability as a guiding principle for modern logistics.

The achievements of food security are specified at a global level as a key element of sustainable development. Energy economy and alternative energies are key challenges for society today, dealt with in a separate chapter. Tens of millions of years ago, biomass provided the basis for what we actually call fossil resources and biomass again is by far the most important resource for renewable energies today.

The efficient complementation and eventual substitution of fossil raw materials by biomass is the subject matter of green chemistry and is comprehensively described. The chapter „Biomass for Green Chemistry“ in particular highlights the potential of sucrose, starch, fats and oils, wood or natural fibres as building blocks and in composites of bio-based plastics and resins. Reduction in greenhouse gas emissions, energy and water usage are examples of the benefits brought about by greener, cleaner and simpler biotechnology processes, comprehensively dealt with in the last chapter „White Biotechnology“. This includes PLA as one biopolymers example for White Biotechnology.

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Pretzels, Plants and Packaging

In time to celebrate the 40th Anniversary of Earth Day - April 22, 2010, Snyder’s of Hanover have announced a breakthrough in pretzel packaging. Snyder’s Organic Pretzel Sticks are now packaged in innovative new Ingeo™ based bags created from 90% plant-based materials.

The bag is created from an innovative Earth Clear™ flexible packaging material developed by Clear Lam Packaging, Inc. Based on Ingeo™ bioplastic, the formulation and construction of the Earth Clear™ packaging enable the bag to perform well without depending on petroleum-based products. In addition, the new packaging requires as little as half the energy to produce as compared to a traditional petroleum-based bag.

Snyder’s Organic Pretzel Stick line, including Organic 8 Grains & Seeds, Whole Wheat & Oat Bran and Honey Whole Wheat, are the first pretzels packaged using this Ingeo™ based renewable packaging material and are available at leading US grocery chains nationwide.

Since their launch, Snyder’s have already been selected as a Silver Finalist in the National Association for the Specialty Food Trade’s 2010 NASFT sofi™ Awards Competition in the Innovation in Packaging Design or Function category. Recognizing outstanding specialty food innovation, the ‘sofi’ award sees intense competition, with 1,570 entries across 31 categories this year. Final judging for sofi Gold Winners occurs June 27-28.

Comprehensive Ingeo™ Product Line now in EarthChoice® Collection from Pactiv

As the National Restaurant Association celebrated its 91st year in Chicago May 23-26, North American based Pactiv Corporation announced the newest additions to its EarthChoice® portfolio of disposable food serviceware. The EarthChoice® collection now captures the very latest in bio-materials performance and innovation with a full range of Ingeo™ products in addition to products made from pulp fiber blends, bagasse, PSM, talc filled polypropylene, and RPET.

The EarthChoice® Ingeo™ collection now includes:

- Ingeo cold drink cups, portion cups & lids. Offered in 7-24 oz sizes with a variety of lids, these offer exceptional clarity, strength durability, and a range of colors and custom printing available.
- Ingeo lined paper hot cups & soup cups. Available in a variety of sizes for both hot and cold beverage needs, these are matched with high heat Ingeo (CPLA) lids available.
- Ingeo hinged & deli clear containers. Also available in a range of sizes.

Pactiv is a leader in the consumer and foodservice/food packaging markets. Their foodservice/food packaging offering has long been one of the broadest in the industry, including both custom and stock products in a variety of materials, and with these latest products, their EarthChoice® collection achieves similar breadth. All Pactiv Ingeo products are ASTM D6400 or ASTM D6868 certified for industrial or municipal compost facilities.
In 1994 at the University of Kassel, Germany, a professorship of ‘Polymer and Recycling Technology’ was created and funded jointly by 29 companies and trade bodies in the region. The chairman is Prof. A.K. Bledzki. Additionally the ‘Innovation Centre for Polymer and Recycling Technology’ is closely connected with the professorship. This member organization is mainly funded by medium sized industrial companies but also by private individuals. The institute concerns itself with scientific and practical problems of plastics technology in the Institute of Materials Engineering (Department of Mechanical Engineering of the University of Kassel).

The investigation of new polymer material systems, the processing of these materials, their characterisation and their testing - these essential activities sum up the main areas of focus.

The course studies concentrate on bio-based polymers and their composites. Materials of natural origin are also used as reinforcing fibres, for example hemp, flax, banana (abaca) and jute. Several research projects in this area are developed every year. The project for the ‘Biopolymers’ research association, sponsored by the German Federal Ministry of Food, Agriculture and Consumer Protection (BMELV) is one example. The focus of the project, which is funded up to approximately four million Euros, consists of seven project units. Especially notable is the amount of interest coming from the industry. In total fifteen companies, including businesses in the region, support the undertaking. The concept aims for a re-use of by-products of agricultural production, the production of cellulose and other processes. With the aid of innovative technologies, petroleum based polymers are to be substituted in technical applications. In addition, bio-based polymer and fibre additives with customized material properties are to be developed.

Example of thin-wall products made of biocomposites

PA6 10% 30% abaca fibre
PP 60% wood flour
PP 40% spelt husk
PLA 30% abaca fibre
PP 40% rice husk
Natural fibres, organic fillers and grain by-products

For approximately ten years, the industry has been displaying increasing interest in the use of renewable raw materials and more specifically in the application of natural fibres. The institute already began research into lignocellulosic fibres and fillers for composite reinforcement in the early 1990s. Essential advantages of lignocellulosic fibres, compared to the glass fibres commonly used today, are their low density, low costs, superior recycling ability, as well as a mostly neutral carbon footprint and with no dependence on the price of crude oil. A completely innovative idea is the application of grain by-products (waste from the wheat industry). Wheat by-products contain a high level of lignocellulosic micro-fibre and are also far more cost-effective than the wood flour conventionally used. This area of research constitutes a further focal point in the field of biocomposites.

Bio-based polymers and their composites

The first studies on bio-based polymers (PLA, PHA, starch etc.) carried out at the institute were already evaluated in the mid-1990s. At that time the focal point of the investigation was on biomedical applications. Over a period of about 10 years the cost-performance ratio also became interesting for technical applications. New formulations of compatibilised blends and high-performance biocomposites with different natural fibres are the focal point of the investigation. By means of extensive research and development, supported by industry partners, a wide spectrum of biocomposites with significantly enhanced property ranges have been developed.

Bio-based thermosets

Common epoxy resins are widely used for glass fibre composites in technical applications. Modern bio-based epoxy resin systems, which are reinforced with natural fibres continue to be a subject of studies at the institute. Epoxy resins are normally synthesized using epichlorohydrin with bisphenol A. It is also possible to substitute the classic epoxy resins with chemically modified fatty acids from plant oils. Clear benefits of bio-epoxy-resins are the bio-based origin, improved skin-friendliness and low toxicity. Engineering thermoplastics

Engineering thermoplastics are an exception within the group of biopolymers and are a very important aspect of the activities of the professorship. For over fifty years several high-performance polymers based on renewable raw materials, such as polyamid 6.10, have been slowly developed. Due to their high processing temperature engineering thermoplastics are almost impossible to process with natural fibres (above 200°C natural fibres are increasingly thermally decomposed) and are unable to adapt to the desired property profile. Thanks to the extensive know-how of the institute and the continuous process optimisation, the reinforcing of engineering polymers (PA6, PA 10.10, PA 6.10, PBT etc.) with customized natural fibres has been achieved and, in consequence, a significant improvement of the mechanical properties was also achieved. For more details see pp 26.

The ground-breaking bio-composites developed at the institute are suitable for various uses in the automobile, furniture, construction and/or electrical industries.

www.kutech-kassel.de
An article about the basics of bio-polyamides (or, more correctly bio-based polyamides) should start with the very basics of polyamides in general. This will help towards a better understanding of this class of materials.

**Basics of polyamides**

In 1927 the world’s largest chemical enterprise ‘IG Farben’ of Germany [closed down after WW II by the Allied Forces] decided to start basic research into high polymers. Shortly afterwards, the largest chemical group in the USA, DuPont de Nemours, assembled a similar research group, headed by Wallace H. Carothers. A few years after the first discovery of a condensation reaction, resulting in a highly viscous substance, Carothers was able to produce the first usable PA 66 filaments from hexamethylenediamine and adipic acid. ‘Nylon’ was born, and after the issue of a patent in 1937 it did not take long before 4 million pairs of nylon stockings per year were being produced. Parallel developments in Germany led to PA6, polymerised from ε-Caprolactam. So the first applications were clearly in the filament and fibre businesses [1] whereas today polyamides can be found in fibres but also in injection moulded and extruded products, as well as in films and blow moulded hollow articles.

Basically polyamides are (in most cases semi-crystalline) thermoplastics which are characterized by a combination of methylene groups CH₂ and amide-groups -NH-CO- in their backbone. Polyamides can be classified into two major groups: AB-polymers (such as PA 6, PA 11 or PA 12) consist of a single basic unit [1, 2, 3, 5].

\[
\text{[NH}-(\text{CH}_2)_x\text{-CO]}_n \quad \text{Where } X+1 \text{ is 6, 11 or 12, or } X = 5, 10 \text{ or } 11 \text{ respectively}
\]

On the other hand AA/BB-polyamide types (such as PA 64, PA 66, PA 69, PA 610 or PA 612) are characterized by two basic units

\[
\text{[NH}-(\text{CH}_2)_y\text{-NH-CO-(CH}_2)_y\text{-CO]}_n
\]

Where the numbers in the polymer’s name give the number of carbon atoms in each basic unit [X and Y+2]: example PA 610 X=10 and Y=8.

**Bio-Polyamides**

Polyamides, in line with the description above, that are partly or wholly made from renewable resources are called bio-polyamides.

And now, even if this point is repeated countless times, it’s well worth saying again: the fact that a plastic material is (partly or completely) biobased is absolutely independent of its biodegradability. And biobased polyamides are, just like petro-based polyamides NOT biodegradable [albeit due to certain heteroatoms in the chain of certain PA types these may be partly biodegradable]. Generally polyamides are meant for rigid and durable applications.

Basically biobased [or partly biobased] polyamides can be made using three different processing principles [2, 6]:

1) Polycondensation of diamines and dicarboxylic acids with elimination of water.

\[
\text{H}_2\text{N-C} \ldots \text{CNH}_2 + \text{HOOC-C} \ldots \text{C-COOH} \rightarrow \text{[...C-NH-CO-C...]} + 2n\text{H}_2\text{O}
\]
Bio-polyamides

Here the dicarboxylic acid can be derived from renewable resources e.g. sebacic acid \([\text{HOOC(CH}_2\text{)}_8\text{COOH}]\) or \(\text{C}_{10}\text{H}_{18}\text{O}_4\) from castor oil. In most cases today the diamines used for bio-polyamides are based on petrochemical resources. Examples are PA610 or PA 610. However, basically it is also possible to prepare the diamine from renewable resources. Lysine, obtained from glucose by fermentation can be converted into 1.5 diaminopentane \([\text{H}_2\text{N(CH}_2\text{)}_5\text{NH}_2]\) and be used to create 100% biobased polyamide 510. PA 1010 can be made with decamethylenediamine \([\text{H}_2\text{N(CH}_2\text{)}_{10}\text{NH}_2]\), also derived from castor oil.

B) Polycondensation of amino carboxylic acids as bi-functional monomers.

\[
\text{HOOC-C} \ldots \text{C-NH}_2 + \text{HOOC-C} \ldots \text{C-NH}_2 \rightarrow […]\text{C-NH-CO-C…}[]_n + 2n\cdot\text{H}_2\text{O}
\]

An example is PA 11.

C) Ring-opening polymerisation of \(\varepsilon\)-Caprolactam \([\text{C}_6\text{H}_{11}\text{NO}]\).

\[
\text{+ catalyst} \rightarrow […]\text{(CH}_2\text{)}_6\text{-NH-CO…}[]_n
\]

If the \(\varepsilon\)-Caprolactam were to be produced in future by fermentation from glucose, possibly via the precursor lysine \([7]\), a biobased PA6 would be possible.

Commercially available bio-polyamides

In the following paragraphs, the most well known or well-described bio-polyamides will be introduced. Some of them have been commercially available for decades, others are quite new and some even not yet available [maybe not even in the foreseeable future]. The following introductions are partly based on information from the individual suppliers, not all of whom have responded to a recent request by bioplastics MAGAZINE.

PA11

PA11 is 100% biobased and made from the monomer 11-aminoundecanoic acid \([\text{NH}_2\text{CH}_2\text{(CH}_2\text{)}_9\text{COOH}]\) based on castor oil. The only producer in the world of 11-aminoundecanoic acid is the French company Arkema (formerly ATOFINA). Their product Rilsan®11, which has been discovered and marketed since as far back as 1947, is widely used in applications requiring resistance and technical skills, such as automobile fuel lines, offshore pipes, etc. [8].

PA 610

PA 610 can be made by a polycondensation reaction from hexamethylenediamine \([\text{H}_2\text{N(CH}_2\text{)}_6\text{NH}_2]\) (mostly fossil based from butadiene or propylene, representing the ‘6’ [hexa] component in PA 610) with biobased sebacic acid from castor oil, representing the ‘10’ component.

There are a number of commercial products available. BASF offer Ultramid Balance®, with a share of 63% biobased carbon. PA610 features in some aspects superior properties compared to polyamide 6 – at lower density. It shows very high impact resistance at sub-zero temperatures, is resistant to outdoor exposure and extremely dimensionally stable because of its low moisture absorption [9].
Basics

Vestamid Terra® is a product line of Evonik, the grade Vestamid Terra HS representing a 63% biobased PA 610 (the ‘H’ standing for hexa). According to Evonik, the material properties of PA 610 can be found between the high-performance polyamide 612 and the standard polyamides PA6 and PA 66.

DuPont have three different PA 610 grades in their portfolio, RS standing for Renewably Sourced. Zytel® RS LC3030 NC010 is an unreinforced, low viscosity grade, developed for injection applications. The medium viscosity grade LC3060 is for injection and extrusion whereas the high viscosity of LC3090 was developed for extrusion applications.

Grilamid® 2S is the PA610 type offered by EMS-GRIVORY. This material is available in no less than 9 grades, including black and naturally coloured impact modified types and 30 - 40 or 50% glass fibre reinforced grades which are in addition heat stabilised.

At the recent Chinaplas trade fair in Shanghai, Rhodia announced the launch of their partly biobased PA 610, named Technyl® eXten. In addition to the properties already mentioned, Rhodia claim for their PA 610 an exceptional chemical resistance, comparable to that of Polyamide 11 and 12, and very high gas barrier properties.

Another company offering PA 610 in different grades is Akro Plastik from Niederzissen, Germany. They have an unreinforced grade and different grades of Akromid S in black and natural with glass fibre contents from 15 to 50%.

PA410

If instead of a hexamethylenediamine [PA 610] a tetramethylenediamine \(\text{H}_2\text{N}(\text{CH}_2)_4\text{NH}_2\) is used for the ‘4’ (tetra) component, again combined with bio [castor oil] based sebacic acid for the ‘10’ component, a PA 410 with approximately 70% renewable content can be produced. DSM introduced their EcoPaXX polyamide 410 in 2009.

PA 1010

Now the principle should be clear. PA 1010 is made of decamethylenediamine \(\text{H}_2\text{N}(\text{CH}_2)_{10}\text{NH}_2\) for the first ‘10’ [deca] component plus sebacic acid for the second ‘10’ component. As decamethylenediamine can also be derived from castor oil, PA 1010 can be produced as an up to 100% bio-polyamide. Commercial products are available from EMS GRIVORY (Grilamid 1S), Evonik (Vestamid Terra DS, ‘D’ for Decal, DuPont (Zytel RS LC 1000, 1200 and 1600) and probably some other suppliers too. Evonik’s material boasts a property profile that closes the gap between long-chained high-performance polyamides like PA 12 and PA 1212 and the shorter-chained standard polyamides PA 6 and PA 66. It is suitable primarily for fibreglass-reinforced moulded compounds.

PA 1012

Not so well known is PA 1012. Here the ‘10’ [amino] component is (as above) decamethylenediamine. The ‘12’ component is a dodecanedioic acid \(\text{HOOC(CH}_2)_{12}\text{COOH}\) with 12 carbon atoms (dodecane for 12). A commercially available product is Evonik Terra DD. As both components can be derived from vegetable oils, this PA 1012 can be up to 100% biobased.

PA 510 (not yet commercially available)

BASF have succeeded in developing a PA 510. Lysine, obtained from glucose by fermentation, can be converted into 1.5 diaminopentane \(\text{H}_2\text{N}(\text{CH}_2)_{5}\text{NH}_2\) for the ‘5’ component. PA 510 is a polyamide based on 100% renewable resources and exhibits a particularly robust and technically relevant performance that make basically suitable for the automotive industry. However, as stated by BASF, currently the PA 510 is a rather expensive specialty PA. Thus a broad application in the cost sensitive automotive industry is not to be expected too soon [bM 01/2010].
In addition BASF point out that due to an eco-efficiency analysis for a typical automotive application (comparing PA 610 and PA 6) which considers ecological and economic aspects, today it is not yet reasonable to substitute PA 6 by PA 610. According to BASF, a biobased plastic is not per se sustainable or better than a petrochemically based plastic. BASF suggest a detailed LCA for each individual case [9].

PPA

Polyphthalamides [PPA] can be made from bio-based decamethylendiamine plus terephthalic acid and are available in different forms from Evonik (Vestamid HT plus) or Ems Grivery (Grilamid HT3), both with up to 50% renewable resources.

Arkema introduced a polyphthalamide [PPA] which is partly based on 11-aminoundecanoic acid from castor oil (see PA 11), up to 70% bio-based. Rilsan HT [High Temperature] is available for extrusion and injection moulding. The extrusion grade is the first flexible high-temperature thermoplastic to replace metal in high-temperature applications. In July 2009, Arkema unveiled Rilsan HT injection resins. Rilsan HT has a melting temperatures of 260°C, for a heat resistance temperature of 180°C.

Other types

A base chemical that can be used among others for polyamides is succinic acid [COOH(CH₂)₂COOH]. Fraunhofer UMSICHT described the production of polyamide 44 or polyamide 4 from succinic acid and its derivates 1,4 –di-amino butane or 2-pyrrolidinone [bM 01/2006 and bM 04/2009].

An amorphous transparent polyamide with a bio-content of up to 54% is Grilamid BTR by EMS GRIVORY. It offers excellent transparency and inherent colour, excellent chemical resistance compared to most other amorphous thermoplastics, high gloss and good scratch resistance, and good adhesion to Grilamid 1S PA1010.

Rilsan Clear Rnew, another bio-based transparent polyamide from Arkema, is designed for the ophthalmic market, such as to make spectacle frames. This resin uses 54% bio-based raw materials [based on Rilsan 11] and offers the same key benefits as the classic Rilsan Clear, such as freedom of design, comfort and durability, excellent transparency and whiteness, flexibility, light weight [density below 1, it floats on water], high elasticity return, remarkable toughness, and excellent chemical resistance.

More polyamides that theoretically can be made from renewable resources (such as PA 6, PA 66, PA 69, PA 64 or PA 34) are described in [7].

As this article cannot claim to cover all bio-based polyamides and copolymers available, bioplastics MAGAZINE is planning a new series of ‘market overviews’ to be started in 2011.

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www.gehr.de
In different committees in Brussels there is an ongoing discussion about how to define and measure the bio-based content of bio-based materials and products. Examples are the CEN/BT/WG 209 M/429 working group - working on a standardisation programme for bio-based products (Brussels, CEN) and the Industrial Task Force on Bio-based Content of Materials and Products (Brussels, European bioplastics).

One of the proposed definitions of ‘bio-based’ is ‘derived from biomass’, which is easy to comprehend. But what does it mean? The total of the plant biomass that is used? And with this not only the carbon atoms, but also the oxygen, hydrogen etc., which are bound in the bio-molecules? Or should we only consider the carbon, after all, the goal is to avoid CO₂ emissions?

The answers to these questions immediately depend on the applied measuring method. One possibility is to follow the US standard ASTM-D6866, which labels the percentage of the ‘renewably sourced carbon’ in the material or product, identified by the ¹²C/¹⁴C method. Only the biogenic carbon counts as biomass here, other constituent parts are not included. Yet carbonates of natural mineral origin get a special treatment: “They are to be excluded”, and consequently don’t raise the ¹²C content.

By choosing the US route, however, one often arrives at unexpected values for the biogenic part so interpreted, which are hard to comprehend at first (see table). How does a material made from 50% PLA and 50% PP become only 36.7% bio-based by measuring the ‘green carbon content’? Due to the fact that in the PLA relatively more oxygen is bound than in PP. But this biogenic oxygen also substitutes fossil carbon (¹²C). Why shouldn’t it count?

Furthermore an optimum saving of CO₂ emissions is not necessarily accomplished by substituting as much fossil carbon in the material or product as possible. The level of CO₂ emission that would be really be saved with the use of bio-based plastics can only be determined by a technically demanding and costly LCA, which takes into account the CO₂ emissions over the entire process chain.

But why not simply measure and label the entire biomass content? The values would be easy to comprehend and could easily be conveyed in communication with clients.

From a technical point of view the calculation of the biogenic mass fraction is not difficult. And furthermore producers would not have to disclose all of their trade secrets about additives applied in small portions. Knowing the biomass share, the content of biogenic carbon can be calculated, and based on that, the ¹²C/¹⁴C ratio can be predicted – with the ¹²C/¹⁴C method the concordance of the theoretically determined values with the reality in the material or product can be controlled any time.

Our recommendation:

Define, measure and label the entire biomass content as bio-based content. Use the ¹²C/¹⁴C method as a quick check of the calculations.

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<table>
<thead>
<tr>
<th>Material Composition, Weight-%</th>
<th>biogenic C-content</th>
<th>fossil C-content</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/PP fossil (50% PLA / 50% PP)</td>
<td>36.7 %</td>
<td>63.3%</td>
</tr>
<tr>
<td>CA* (acetic acid fossil), average¹</td>
<td>54.5 %</td>
<td>45.5 %</td>
</tr>
<tr>
<td>Ecovio (45% PLA/55% Ecoflex)</td>
<td>39.4 %</td>
<td>60.6 %</td>
</tr>
<tr>
<td>WPC (70 % wood / 30 % PP fossil)</td>
<td>57.6 %</td>
<td>42.4 %</td>
</tr>
<tr>
<td>WPC (30 % wood / 70 % PP fossil)</td>
<td>19.9 %</td>
<td>80.1 %</td>
</tr>
<tr>
<td>WPC (70 % wood / 30 % PVC fossil)</td>
<td>75.2 %</td>
<td>24.8 %</td>
</tr>
<tr>
<td>WPC (30 % wood / 70 % PVC fossil)</td>
<td>35.8 %</td>
<td>64.2 %</td>
</tr>
<tr>
<td>Composite Material (40% GF / 30% PLA / 30% Ecoflex)</td>
<td>44.3 %</td>
<td>55.7 %</td>
</tr>
<tr>
<td>Composite Material (40% NF/60% PP fossil)</td>
<td>27.9 %</td>
<td>72.1 %</td>
</tr>
</tbody>
</table>

---

1: Data from Rodion Kopitzky, Fraunhofer UMSICHT

---

Biogenic Carbon-content for different Bio-based Plastics and Composites:

The following average (total) carbon contents served as a basis for the calculations:

Polylactide acid (PLA): 50%, Polypropylene (PP): 86%, Polyvinylchloride (PVC): 38.4%, Ecoflex: 62.9%, Cellulose Acetate (CA)*: around 50%¹, wood and natural fibres (NF): 50%, glass fibre, talcum, other minerals according to ASTM-6866 also natural mineral carbonates: 0%

*: Cellulose Acetate (CA): carbon content depends on substitution level from acetic acid, average here 2.5¹

¹: Data from Rodion Kopitzky, Fraunhofer UMSICHT

---

Opinion

How to Measure the Bio-based Content

A contribution to the discussion by

Michael Carus, CEO
and Lena Scholz, staff scientist,
bio-based materials,
nova-Institut GmbH, Hürth, Germany

and both representatives of the European Industrial Hemp Association in the committees mentioned
The Bioplastics Award will be presented during the 5th European Bioplastics Conference, December 1/2, 2010, Düsseldorf, Germany

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2. Why you think this product, service or development should win an award
3. What your (or the proposed) company or organisation does

Your entry should not exceed 500 words (approx 1 page) and may also be supported with photographs, samples, marketing brochures and/or technical documentation.

More details and an entry form can be downloaded from www.bioplasticsmagazine.de/award
Ramani Narayan

**bm:** Dear Professor Narayan, when and where you born?

**RN:** In February 1949 in a small town near Bombay (today Mumbai) in India.

**bm:** Where do you live today and since when?

**RN:** In Okemos, Michigan, USA, not far from Michigan State University. I came to the USA from India in 1979 to start work as a post doctoral fellow at Purdue University.

**bm:** What is your education?

**RN:** I did my PhD in India in organic chemistry with a biopolymer focus. I studied chemistry and polymer engineering.

**bm:** What is your professional function today?

**RN:** At MSU I am a University Distinguished Professor in the department of chemical engineering and material science. In addition, I am the Scientific Chair of different committees and organizations such as ASTM, ISO, etc.

**bm:** How did you ‘come to’ bioplastics?

**RN:** Way back in 1986/87 when almost nobody did any research and no [zero] products were in the market. I was research professor at Purdue University in West Lafayette, Indiana at the laboratory for renewable resources engineering and I wanted to develop a new area of research that was different and futuristic and few people were working on. At that time, farmers in Indiana were looking for new value added uses from their corn and soybean crops. So I teamed up with them to explore the use of corn starch and soybean oil to make value added bioplastic products. I was one of the organizers of the First Corn Utilization Conference held in 1987 where I presented a paper on Materials Applications. At that time the focus was on ‘biodegradability’. Interestingly, I published my first invited paper titled ‘Environmentally Degradable Plastics’ in 1989 in the premier German magazine KUNSTSTOFFE. In that paper I talked about the need to document complete biodegradability and link it to composting disposal environment, which is still relevant today.

**bm:** What do you consider more important: ‘biobased’ or ‘biodegradable’?

**RN:** Biobased carbon as opposed to fossil carbon has a greater impact and applicability – offers the potential for reducing the material carbon footprint which is the burning issue of the day. I envision that in the future most plastics will be made from a bio-renewable feedstocks. On the other hand, biodegradability in concert with the target disposal environment like composting is a useful and viable end of life option. Biodegradability is good for selected product applications where it contributes added value.

**bm:** What was your biggest achievement (in terms of bioplastics) so far?

**RN:** There are two: One is in helping develop standards for biodegradation of plastics in different disposal environments as part of an ASTM committee which I chair. The second one was in developing the value proposition for bio-based plastics in terms of material carbon footprint reductions and the $^{14}$C methodology to quantify biobased content which is now codified in the ASTM standard D6866. And, if I may say the PLA technology that today forms the basis for Natureworks and others was first initiated and developed in my laboratory at MSU.

**bm:** What are your biggest challenges for the future?

**RN:** It is to help achieve clarity and consensus about the biodegradability concept. What and when companies can claim their product is biodegradable and they specify the target disposal environment as well as the time to complete biodegradation in the selected disposal environment. I am equally challenged to do research, educate and push for bio-renewable based products where material carbon footprint reductions value proposition can be articulated and communicated to the public at large.

**bm:** What is your family status?

**RN:** I’m married to my wife Homa and we have two sons. Rishi [27] is a chemical engineer and he is an entrepreneur. Rohit [22] has a degree in Economics and one in German language. Both were at the University of Michigan.

**bm:** What is your favorite movie?

**RN:** I’m not a big movie watcher and would rather be out playing golf or tennis.

**bm:** What is your favorite book?

**RN:** I enjoyed reading books by Michael Crichton and Dan Brown. But more often I end up reading the scientific literature.

**bm:** What is your favorite (or your next) vacation location?

**RN:** I am not a fan of taking vacations. Once in a while I do take a few days off or if my wife comes with me on conference trips, we catch a few historical sites.

**bm:** What do you eat for breakfast on a Sunday?

**RN:** I love wholesome orange juice, cereals but occasionally indulge in a nice, big Indian breakfast/lunch.

**bm:** What is your ‘slogan’?

**RN:** I don’t really have one – Maybe “Live and let live”

**bm:** Thank you very much. 

**MT**
PLA Beverage Bottle Presented in Austria

The Austrian pioneer company NaKu (from Natürlicher Kunststoff = natural plastic) has offered starch based bags for fresh produce since 2007. Now they arranged for fresh moments at the VIENNA BIO-POLYMER DAYS on May 19 and 20, 2010. For the first time in Austria the conference delegates can enjoy a flat mineral water from bottles made from a natural plastic material. A unique co-operation project between NaKu and the beverage bottling company Vöslauer (from Bad Vöslau, Austria) makes it possible to present the marketability to a broad public. "We want to address specifically companies that want to strike a new path in terms of beverage packaging," says Johan Zimmermann, Managing Director of NaKu.

The innovative NaKu beverage bottle is made from PLA, derived from vegetable starch and completely biodegradable. Its mechanical properties and processability are comparable to PET, as stated in a NaKu press release. Besides its climate friendly production process and better CO₂ balance, The Viennese entrepreneur emphasizes the end of life options, such as mechanical recycling, thermal (energy) recovery and composting in a commercial composting plant. "All our products are free of harmful substances such as bisphenol A, antimony or acetaldehyde. This makes them particularly interesting for the food and beverage industry," confirms J. Zimmermann.

And he is convinced about this promising innovation of packing natural produce in natural plastic. "Natur & plastics - it works!"

www.naku.at
www.voeslauer.com

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deutschsprachiges Seminar (German language seminar)

Blasformen von Biokunststoffen
In Kooperation mit der Dr. Reinhold Hagen Stiftung
1./2. September, Bonn

Details in Kürze unter www.bioplasticsmagazine.de/blasformseminar

- Streckblasen von Biokunststoffen (wie PLA)
- Extrusionblasen von Biokunststoffen (wie PLA/Polyester Blends, PHA, Bio-Polyamiden etc.)
- verwandte Themen wie
  - Barriere
  - Verschlüsse
  - Etiketten
  - Fragen der Entsorgung
  - und vieles mehr ...
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