Computer manufacturer Fujitsu utilizes renewable raw materials for their computer mice (photo: FKuR)

Bioplastics

Visions and Investments. Brand-name companies like Coca-Cola, Danone, Nestlé or Procter & Gamble have discovered bioplastics for themselves. Their first biopackagings are on the shelves – with leading brands, not just for test runs. High investments in a wide variety of bioplastics give evidence to the fact that many materials are finding a market – not just for use as packaging. The name of the game is functionality, and it applies especially to biodegradable and high-performance engineering bioplastics.

HARALD KÄB

Good ideas quickly find lots of believers. It is good that people like to copy very good ideas, because that is how they get even better. "Conceptual innovation", the idea by which computer giant Apple triggered an InfoTech wave with iPhone and iPad, could, figuratively speaking, be applied to Coca-Cola, too. When Coca-Cola introduced the "plant bottle" for its brand-name soft drinks and packaging in 2009, the company declared its intention to change its plastic beverage packaging, step by step, from fossil PET to entirely bio-based PET. PET is still their preferred plastic, because it is very important for the company that their packaging can be recycled. In the long-term, in the end, that is, PET should be produced from non-food biomass feedstocks. Coca-Cola began by using bio-based monoethylene glycol (MEG) for its 500 ml cola bottle, and other Coca-Cola beverage brands followed. At the same time, they increased the rPET (recycled PET) content in the bottles. Bio-based content in this first step was 30 wt.-%. According to company estimates, this first step eliminated some 30,000 t of CO_2 emissions in 2010, or approx. 15 % per bottle.

This "green" monomer building block in PET also convinced the makers of Heinz Ketchup to cooperate with Coca-Cola and join in their effort to leap the hurdles in their path. Coca-Cola intends to equip some 2 billion bottles this year in this way. Heinz is making a start in 2011 with 120 million bottles, and by 2020 their current product range will switch to the "green" PET bottle (**Fig. 1**). Since 2010, Danone's affiliate Volvic has been marketing its 1.5 liter water bottle in this form. This obviously popular approach has also heated up the technological competition: less than two years after Coca-Cola, PepsiCo has declared they are close to fulfilling the goal of producing a 100 % bio-based PET bottle from food wastes. There are various methods for producing the second monomer building block, terephthalic acid (TPA), from biomass. In a just few years, they intend to introduce the "ultimate Bio-PET bottle" for Pepsi-Cola beverages.

Bio-based and recyclable – this approach was unheard of, prior to Coca-Cola. Extremely important in this connection was the pioneering work done by Braskem of São Paulo, →

Fig. 1. Heinz for Ketchup and Coca-Cola for various brands: Both are cooperating to use bio-based PET (photo: Coca-Cola)

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Fig. 2. Danone's PLA yogurt cup is recyclable and can help reduce greenhouse gases (photo: Danone)

Brazil. For a year now, they have been transforming bioethanol (fuel) from sugar cane into bioethylene on an industrial scale, thereby turning it into a platform for numerous recyclable plastics. The infrastructure for recycling PET or polyolefins, such as PE, has become established to a meaningful degree in many countries of the world. Whether biogenic or fossil versions are recycled is technologically irrelevant, since they are 100 % compatible. Ecology and, more recently, resource politics regard recycling as an important tool for achieving greater resource efficiency and sustainable development. After all, the need to conserve applies just as much to renewable raw materials as it does to fossil materials: Unless they are used efficiently, there will not be enough of them. Reuse and recycling of products are the prerequisites for cascade use. This approach, together with product design aimed at longevity and recyclability, is the key to significantly improved resource efficiency. In the main, laws that dictate recycling rates for product wasters, e.g., for packaging, electrical devices or automobiles, are advancing it. Quotas for the use of recyclate and biomass would be a logical extension of this way of thinking.

Danone is yet another company in the food industry that is betting on the concept of "bio plus recycling". Not only is Danone using semi-bio-based PET for the plastic bottles of its Volvic affiliate, but BioPE for the plastic bottles containing its yogurt drink, Actimel, as well, and Ingeo PLA (polylactic acid) for its Activia brand yogurt **(Fig. 2)**. Both are very successful, well-known brands of yogurt. For the chemical process envisaged to recycle PLA – hydrolysis to the monomer and repolymerization – the corresponding logistics and infrastructure still have to be created. The quantity is still too small for economical operation. Danone Germany has already proven that PLA cups can be specifically sorted out in recycling plants, and that PLA can be recycled – at this time by Galactic in Belgium only. As for other brand-name companies, Danone regards improving environmental performance an important goal. Using thin-walled PLA cups can reduce packaging quantity. Since corn is also used instead of crude oil, the company can point to considerable reductions in greenhouse gas emissions and fossil energy. Not all the criteria in the published ISO-conform ecobalance look better – the effects of fossil vs. agricultural origin on the individual indices are much too different. But when climate protection and resource consumption are appropriately weighted, considerable progress has been made. Further optimizing, e.g., by recycling instead of energy recovery, is quite possible, as calculations indicate. Together with the WWF (World Wide Fund for Nature), Danone has been active for the sustainable production of agricultural raw materials. The acreage used for producing the PLA cups is certified according to EU sustainable biofuels guidelines. The company is strongly engaged in bioplastics for packaging.

More than five years ago, automobile manufacturer Toyota published its vision of bio-based plastics in automobiles and has been implementing it consistently since then. Toyota is planning to substitute significant amounts of fossil plastics in this art and manner. In models such as Prius **(Fig. 3)**, its new hybrid SAI or Lexus 200, the interiors already consist of up to 60 % bioplastics. From foamed seats made from vegetable oil-based polyurethane, to fabric covers or foot mats from partially bio-based polyester (PTT) or to BioPET for instrument panel skin – Toyota is showing what can be done already. Among other companies with declared goals for the use of bioplastics, we find the cosmetics producer Shiseido or consumer goods giant Procter & Gamble (P&G). According to P&G, no plastics will be used in the long run that are not made either from sustainably sourced non-food renewable raw materials or from recovered recyclates. Using Baskem's BioPE to package Pantene, P&G's leading brand of shampoo, is their first step in this direction. In June, Nestlé named similar ideas as company goals, thereby emphasizing the role of drop-in bioplastics, i.e., that change the raw material base of commercial plastics. Nestlé is already using PLA and starch-based plastics. In addition to the wish to diversify their raw materials base and move toward more recycling, users are motivated by bioplastics' contribution toward reducing greenhouse gases. Walmart – the world's largest trading company and a pioneer in the use of biopackaging – announced in April that it had already saved 5,000 t of CO_2 emissions by using PLA.

If we translate the announcements and visions of the companies mentioned into plastics market volume, then it adds is to something on the order of 5 million t. That is five times the current global bioplastics production capacity. The decisions of large users will have a decisive influence on the supply chain. Whoever has the capital to conquer this commodity market as a pioneer will invest in bio-based monomers and bioplastics. Beverage producers, such as Coca-Cola and PepsiCo are getting into the action and becoming manufacturers of packing materials.

For the badly battered manufacturers of biofuels, such as bioethanol, fantastic new perspectives are opening up as manufacturers of chemical raw materials. European energy and biofuel policy is, to be sure, not prepared for this. It continues to promote combustion as the only direct use of such valuable raw materials as bioethanol. This discriminates against the industrial use of agricultural materials by favoring energetic use. If this is to be changed, the industry will have become politically involved. Then it will be important to demonstrate the advantages of cascade use, such as improved

Fig. 3. Toyota is subsequently increasing the use of bioplastics for interior car parts (photo: Toyota)

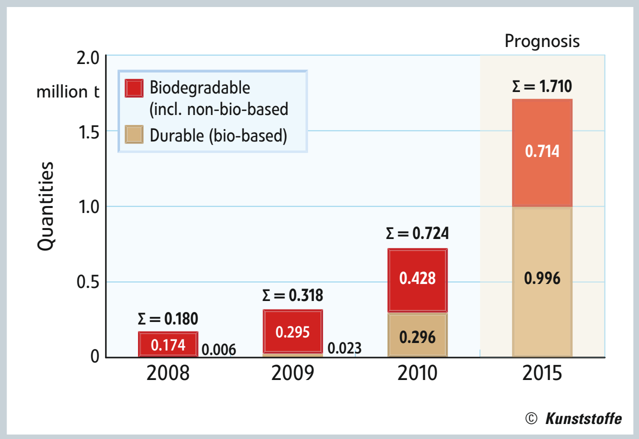

Fig. 4. Worldwide production capacities of bioplastics (as of May 2011) (source: European Bioplastics/FH Hanover)

efficiency in the use of agricultural land and raw materials, or from the prospects of far higher value and employment, as well as a better ecobalance. The Wuppertal Institute for Climate, Environment and Energy GmbH, Wuppertal, Germany, is studying this approach intensively [1] and, therefore, calling for an integrated strategy for the material and energetic use of biomass [1, 2]. More than 90 representatives of bio-based industry have subscribed to similar calls for such a policy, based on an initiative by M. Carus [3]. Otherwise, European plastics manufacturers stand to suffer severe disadvantages in the global competition for bioplastics.

Growth Statistics

There are no official statistics on bioplastics, but various companies provide studies of the commercial market. European Bioplastics e. V., a trade association located in Berlin, publishes data on the production of thermoplastic bioplastics at regular intervals [4]. These do not include the cellulosic materials that have been in use for many years on a million-ton scale in saturated markets. Also excluded are thermosets such as polyurethane or epoxides with bio-based content, and plastics reinforced with natural fibers or filled with sawdust (WPC). The latter do not fit the definition of bioplastics.

In May of 2011, the association stated that global capacity for producing bioplastics would more than double between 2010 and 2015. Right this year, we may cross the one-million-ton threshold. Having achieved 700,000 t in 2010, that means that production capacities for bioplastics should reach 1.7 million t by 2015 **(Fig. 4)**. In 2010, the bioplastics branch manufactured approx. 400,000 t of biogradable and 300,000 t of non-biodegradable bio-based materials **(Fig. 5)**. This relationship will – given widespread growth – invert in the coming years. Simultaneously with their market debut, drop-in bioplastics will be manufactured in relatively large dimensioned plants. Since they involve no new properties, producers of bioplastics such as BioPE will have to orient themselves strongly on the market price for fossil models. That is why they will rely on the greater economy that comes with large facilities.

Viewed in terms of market segments, the branch is still on the threshold of development: Bioplastics comprise less than 1 % of the total plastics market of some 250 million t (2010). Their average growth has ranged between 20 and 30 % annually in recent years. European consumption is running just over 200,000 t (2010). Further growth chances are considered excellent by producers themselves as well as by numerous studies. With a dose of optimism and a strong tailwind from policy measures, market volume in Europe can reach 2 million t in 2020, European Bioplastics estimates. It is quite hard to predict the size of achievable potential, since it depends on so many factors. The Pro-Bip Study in 2009 by the University of Utrecht, Netherlands, found that – from a purely technological standpoint – up to 90 % of all plastics could be shifted from oil and gas to renewable raw materials.

Biodegradable bioplastics are utilized mainly where they bring advantageous technical properties or special functions to the product. At the top of list we find compostability and mechanical parameters, further down are barriers and glossiness, to some extent good electrostatics or printability without pretreatment, or pleasant haptics. Secondary effects, such as low handling or disposal costs, thanks to organic recycling, can be an additional motive for use in the B2B area. For drop-in bioplastics, on the other hand, environmental communication is the main thing. Users are betting that consumers will see their (brand) image as positive. CSR (corporate social responsibility) programs and membership in listed sustainability indexes can be brought to play. The improved ecological properties that would relativize higher purchase prices – a usually low carbon footprint, less energy consumption – cannot be cashed in on yet. Especially for brand-name producers, the value of brands and listings, as well as consumer loyalty, are important motivators for more bioplastics.

Materials and Product Development

Since the author's last report, there has been a flood of announcements concerning new products and investments. The following selection thus cannot provide more than a rather subjective and limited impression of the progress made in the meantime. Included in it are bioplastics which are, according to general agreement among the relevant industrial associations, either biodegradable and compostable and/or bio-based. Nearly all bioplastics that fit this definition contain a considerable amount – upwards of approx. 30 wt.-% – of renewable raw materials.

Biodegradable bio-based plastics: These include starch blends consisting of thermoplastically modified starch and other biodegradable polymers, as well as polyesters, such as polylactic acid (PLA) or poly- →

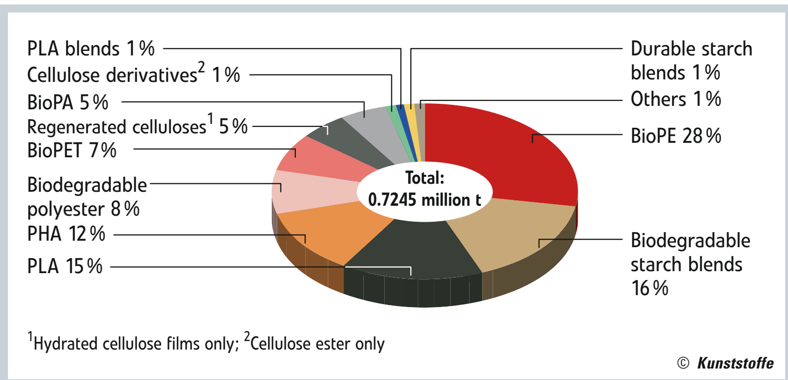

Fig. 5. Worldwide production capacities of bioplastics in 2010 arranged according to materials type (source: European Bioplastics/FH Hanover)

hydroxyalkanoate (PHA). In contrast to cellulose materials, such as regenerate cellulose or certain cellulose acetates also belonging to the category, they have not been available on a scale suitable for production until recently. Most current applications involve short-lived film products, such as FMCG packaging, agricultural films, carrier bags and biowaste sacks. Whereas the producers of starch materials emphasize the compostability of their products, PLA can also be modified to non-degradable types by specific combinations of isomers or by compounding. The market leader, NatureWorks LLC of Minnetonka, Minnesota, USA, hopes to succeed with new PLA types with improved technical properties that will make them suitable for fiber manufacture and injection molding. Samples will be available starting in 2012, and commercial production has been announced for 2013. The decision to build a second industrial facility has not yet been finalized, but it will probably be located in Asia. Meanwhile, additional PLA manufacturers are searching for partners to expand production and further technological development.

A long list of companies are investing millions in bio-based butane dicarboxylic acid (succinic acid) or butanediol. These versatile chemicals can be utilized as monomers especially for producing biodegradable polyester. Purac Biochem of Gorinchem, Netherlands, and BASF SE of Ludwigshafen, Germany, began negotiations in July for a joint venture to produce succinic acid. One step ahead of them, the Thai PTT Group and Mitsubishi Chemical Corporation (MCC), will build a fermentation plant for 36,000 t of the monomer and 20,000 t of polybutylene succinate (PBS), the polymer produced from it. The technology for fermenting succinic acid will be supplied by BioAmber Inc. of Banzancourt, France, and Myriant of Quincy, Massachusetts, USA. Moreover, MCC is working together with Genomatica of San Diego, California, USA, on the direct fermentation of butanediol. Novamont of Novara, Italy, wants to enter a joint venture with Genomatica to build a butanediol plant. Bio-based butanediol and butane dicarboxylic acid are opening up a wide spectrum of possibilities. Even high-performance, durable engineering plastics such as polybutylene terephthalate (PDT) can thereby obtain a green building block.

Fig. 6. Multi-layer films from various bioplastics and metallized surfaces have decidedly improved barrier behavior in, e.g., tea packages (photo: Innovia)

Novamont and its partner, Eni of Rome, Italy, are investing approx. EUR 500 million in the construction of a chemical complex in Sardinia. Vegetable oil-based monomers will be manufactured there that are suitable above all for polyesters as well as for additional bio-based chemicals for a variety of applications. In reciprocal partnerships with numerous film processors, companies like BASF, Novamont, FKUR Kunststoff GmbH, Willich, Germany, or Innovia Films of Wigton, England, (**Fig. 6**), are constantly developing new types of biodegradable multilayer films or paper composites with improved properties. For the latter, BASF has invented an especially suitable laminating glue and recently marketed it.

Manufacturers of starch materials, such as Novamont, Cereplast of El Segundo, California, USA, Cardia Bioplastics of Mulgrave, Australia, or SPhere-Biotec of Paris, France, are aiming their products at the market for biowaste sacks and compostable carrier bags. They are not doing this just to please their users: The EU Commission which rejected the ban on non-biodegradable single-use carrier bags that France was pushing for in 2005 has, in a second attempt, ordered a public consultation – this time in reaction to an Italian law banning them since 1 January. The poll will investigate the acceptance of political measures aimed, on the one hand, at reducing the use of single-use shopping bags and, on the other, at advancing bioplastics technology, in particular, that of biodegradable plastics. Plastic bags and sacks are being used by the billions and on a million-ton scale in Europe. This application could become the first market for bioplastics with strong political support. The results of the poll and the conclusions drawn by the EU Commission were not yet available when this report went to press.

By now, there is hardly a country left in the world where considerations for regulating plastic bags have not been formulated. They are a typical throwaway product with a high level of littering and are considered especially bad for the ecology. Several countries and numerous large cities have therefore slapped taxes on them or limited their use. In Germany, the use of single-use shopping bags has been strongly reduced in favor of reusable ones, usually available only at appreciable cost. Leading chain stores, such as Aldi (**Fig. 7**), Rewe or Tengelmann-Kaiser are already offering biobags in cities like Berlin. Everywhere in Europe, especially in Belgium, Germany, Italy, Austria and The Netherlands, bio-based and biodegradable carrier bags are on the march. However, their market segment is still far below 5 % and thus quite small. A number of plastics processors, such as BioBag International of Hofsveien, Norway, SPhere of Paris, France, Wentus Kunststoff GmbH, of Höxter, Germany, or Victor Güthoff & Partner GmbH of Frechen, Germany, have successfully specialized in biobags. Starch materials are not the only ones used. Mirel-PHA types suitable for films also became available recently. Even relatively brittle PLA can be used to produce carrier bags by compounding it appropriately. Cerestar of El Segundo, USA, announced in May that it would set up the production of starch materials in Assisi, Italy.

Bio-based polyolefins and PET: The currently most widely used non-biodegradable standard plastics, PE, PP and PVC, can also be manufactured from renewable raw materials. The synthesizing processes often run via bioethanol manufactured as biofuel on a multi-million ton scale. BioPE is already being produced on a commercial scale; BioPP and BioPVC will

Fig. 7. The bio-carrier bag is gaining ground in the market: conventional single-use shopping bags are subject to massive political pressure (photo: BASF)

soon follow. Since the entire value chain only needs to be altered at the starting point, they are called "drop-in" bioplastics. Whether fossil or renewable based – the product is identical from an engineering point of view. New applications require no new developments such as are required for biodegradable plastics – which clearly shortens the time to market.

Braskem, until now the only manufacturer, supplies bio-based PE-HD and PD-LD grades as well as green ethylene. Two years from now, Braskem will put 100 % bio-based PP on the market, and they intend to invest in bioethylene on a large scale. Dow of Midland, USA, and Mitsui of Tokyo, Japan, announced plans for a joint venture in July that is also intended to supply these types of bioplastics on a large industrial scale.

Automobile maker Toyota is planning to produce bio-based PET products for some of its interior paneling. It will be used for the trunk lining in their new Lexus CT 200h that was introduced in early 2011. Subsequently, both the number of vehicles in which this material is installed, as well as the amount of material per vehicle, will increase continually. To this end, Toyota affiliate Toyota Tsusho Corporation (TTC) has initiated a 50:50 joint venture with the Man-made Fiber Corporation of Taiwan. Greencol Taiwan Corporation (GTC) has been founded to manufacture 100,000 t of BioMEG to be used for PET, starting at the end of 2011. Bio-based PET for fiber applications is also envisioned by Teijin Fibers of Tokyo, Japan. Commercial production should begin in Japan in April 2012. In the first year, approx. 30,000 t will be available for technical and textile applications. They intend to expand production successively up to 70,000 t by the third year.

Bio-based engineering plastics: They comprise a large group that includes many special polymers for all kinds of uses (e.g., automobile, building construction and electronics). Typical engineering applications include, e.g., textile fibers (for seat covers and rugs), foam materials for seating, housings, pipelines, hoses, construction elements and covers. Useful life generally lasts for several years, so that they can be termed durables. For this reason, biodegradability is neither desirable nor common.

Comparatively speaking, very high performance bio-based polyamides, mostly on a castor oil basis, have been on the market for a long time. The 9, 10 and 11 grades are available in numerous varieties from the manufacturers. The demand for them has grown fast in recent years. Some of them are used in areas where the capabilities of these special plastics are scarcely required. In engineering polyesters, such as PTT or PBT, one of the building blocks is usually replaced by diols from renewable raw materials (often propanediol, also ethylene glycol and butanediol). The monomer 1.3 propanediol produced by DuPont in cooperation with Tate and Lyle of Loudon, USA, is in strong demand, so that a 35 % increase in capacity was announced in May. BioPDO is also used in polyester materials such as Toyota uses for the interior of its Prius. For bio-based polyurethane (PU), mostly sugar and vegetable oil derivatives are used **(Fig. 8)**. Rampf Giessharze GmbH & Co. KG of Grafenberg, Germany, intends to produce a large amount of its materials from renewable raw materials by 2013. Their first biopolyol-based products are already on the market, such as a grommet used in cars and made from a bio-plastic based on rapeseed oil-polyols. Bio-based polyol components are currently offered by a growing number of PU manufacturers. Polyepoxides can also consist partly of renewable raw materials by using bio-based epichlorhydrin (from glycerin).

Avantium of Amsterdam, Netherlands, has announced a strategic partnership with Solvay of Brussels, Belgium, for the purpose of marketing commercially the technology developed to manufacture the novel PEF (poly-ethylene-furan) polymer, a PET-analog. Instead of terephthalic acid (TPA), they use furandicarbonic acid obtained from wood by chemical processes. PEF has properties similar to those of PET and can be produced 100 % bio-based in combination with BioMEG. An additional advantage comes from avoiding any significant conflict of interest with food over raw materials. The materials goals of beverage producers Coca-Cola and PepsiCo have also led several companies to give strong consideration to producing bio-based TPA.

PMMA (e.g., Plexiglas) from renewable raw materials is ever closer to becoming a reality. Arkema of Serquigny, France, will supply bioacrylic acid beginning the middle of next year, for medical applications at first. Plastics specially developed from it exhibit extreme resistance to shock. Biotech companies, such as Rennovia of Menlo Park, USA, have reported great progress in the chemocatalytic manufacture of bio-based adipic acid, a base product of polyamide 6 and 66. Vinyl acetate for producing EVA is another goal at the development departments of chemical companies. Computer manufacturer Fujitsu is now utilizing combinations of wood materials, such as arboform, and bioplastics, such as biograde, to market computer mice **(Title photo)** made from renewable raw materials.

Other (Bio?)Plastics: The assignment of polymer material types to the concept of bioplastics has not yet been clarified univocally, for which reason they are interpreted differently. Hybrid bio(plastics) are mixtures of starch and polyolefins with a high starch content (20 to over 50 %), but not →

Fig. 8. Bio-based polyurethanes are being used in more and more running shoes (photo: Käb)

biodegradable (e.g., by Cerestar or Cardia Bioplastics). Wood plastic composites (WPC) are polyolefins highly filled with sawdust. Natural fiber-reinforced plastics are combinations of natural fibers with fossil-based PP, polyesters or polyepoxides, among others. Matrix materials can also have a bio-base origin in the future. Research into the production of bio-based monomer versions of polymers is running at top speed worldwide. The same holds true for polymer and plastics development, with the result that the variety of bioplastics or plastics with a bio-based component will continue to grow quickly. The borders between bio- and normal plastics are fuzzy and determined only by definition.

Conclusions

The innovative strength of manufacturers, the sensitivity of users for new materials trends, consumers who give thought to their offspring, and politicians, too, in search of voters – all of them will ensure that the materials of the future are far "greener" than today's. It follows an inner logic that can be stretched for a while, but not the results. This shift is not only being prepared conceptually. The ideas for sustainable materials are already on the market. Where just a few years ago, they were merely niche products, today they are the world's best known brands. The bioplastics industry is demonstrating more and more of its capabilities and potential. Those who fail to position themselves soon and stake out their claims could just come too late.

The bioeconomy is offering fantastic prospects for the plastics industry to free itself more and more from its dependence on fossil raw materials. European companies are running up against new challenges: While the chemical and the plastics industry shift production sites to foreign oil drilling holes, the access to renewable raw materials in the large volumes required will be a rough road, too: South American sugar is especially competitive. European bioenergy and -fuel policy is looking more and more like a flawed development, because it prevents resources such as bioethanol from being used as chemical platforms. Globally active companies can deal with the raw materials shift in the plastics industry much better than the branch's numerous KMUs. The course is being set: It is being decided today who will be able to supply in five to ten years, where production will take place, and how strong supply connections will be. ■

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The Author

HARALD KÄB is the director of narocon, a consultancy for green chemistry and bioplastics, in Berlin, Germany.