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biobased performance materials

Large-scale use of biobased materials getting closer and closer

Cost-effective production of biobased bulk chemicals

Suitable biobased plastics for printer panels

Colophon

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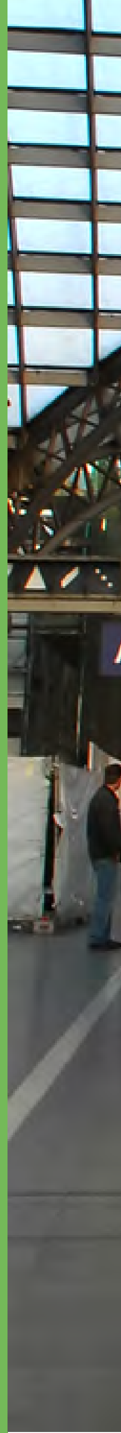


Large-scale use of biobased materials getting closer and closer

The biobased economy is in full swing in the Netherlands with a rise in recent years in the use of residual side and waste streams and biofuels as well as an increase in the development and application of biobased materials. However, significant progress still needs to be made in crucial areas.

Jacco van Haveren

Karin Weustink

The biobased economy is receiving quite some of encouragement. The business community and government authorities are developing key technologies in public-private partnership programmes to help the biobased economy on its way. 'The government is committed to ensuring that initiatives in this area are driven by the business community,' says Karin Weustink of the Dutch Ministry of Economic Affairs. 'In this, the government fulfils

'The government has succeeded in putting the biobased economy on the map'

a facilitating and stimulating role.' Special attention is being given to the three core or top sectors that play a crucial role in the biobased economy: the agricultural sector, the chemical sector and the energy sector. The agricultural sector produces renewable raw materials that can form the basis of biobased materials, chemicals and bio-energy. The government has brought these core sectors into dialogue with one another so that they can join forces to get the biobased economy on the road.

Optimal use of biomass

'The government has succeeded in putting the biobased economy on the map,' says Jan Noordegraaf, General Manager at Synbra Technology in Etten-Leur. 'Unfortunately, the crisis of 2010 and 2011 caused some delay as companies turned away from green chemicals en masse.' It is therefore a good thing that Gerda Verburg – former Dutch Minister for Agriculture, Nature preservation & Fisheries – funded in 2009, somewhat against the tide, the Biobased Performance Materials research programme. Five years later, the BPM programme proved to be a success, even setting an example of how collaboration can be fostered within the golden triangle. According to Weustink, more and more companies are investing in biobased research and product development. And more and more biobased products are coming onto the market. The main focus is on high-quality use of renewable raw

Christiaan Bolck

Jan Noordegraaf

materials and greener production processes. In July 2014, Minister Kamp send a letter to the Dutch parliament, setting out his view on the optimal use of biomass. In this ‘cascading letter,’ he describes how added value should be maximised for the various fractions of biomass: not just energy but also food, materials and chemicals. This significantly increases total value and ensures a fairer distribution. Weustink (Deputy Director of the Biobased Economy Directorate) reports, ‘The cascading letter was well received by the Dutch Parliament. The use of biomass will play an important part in the Government’s long-term aim to reduce CO_2 emissions. This provides room and flexibility needed for further development of the biobased economy.’

Industrial policy

According to Weustink, the government is investing heavily in a sustainable economy through specific subsidies and programmes. As she explains, ‘We are currently working on a new eight to twelve-year R&D programme for the biobased economy, part of which is a separate programme line for materials from renewable resources.’ Despite these positive developments, Noordegraaf still has some criticism regarding the government’s efforts. It should and can do much more, he thinks. He is calling for a reward, for

‘It is wrong that CO_2 emissions do not incur costs, but a properly thought-out national tax on the emission of this greenhouse gas could redress the situation’

instance, for those able to avoid producing CO_2 emissions. ‘The avoided costs related to CO_2 emissions in the production of biobased materials are not reflected in the price of the product,’ he explains. ‘It is wrong that CO_2 emissions do not incur costs, but a properly thought-out national tax on the emission of this greenhouse gas could redress the situation.’ Noordegraaf also sees a role for the government in stimulating the cost-effective, large-scale production of biobased materials. According to him at present it appears not yet to be possible to scale up production. He continues, 'The Netherlands does not have a successful industrial policy. There is a lack of political will; amongst others it is claimed EU rules on state aid prevent government to implement this crucial point. However, other countries are able to find solutions to this problem through the clever use of regional funds.'

Via first generation to second generation

In addition, there is a persistent misunderstanding among many stakeholders. During the development, they want to make immediate use of second or even third generation raw materials, such as organic waste. However, there are no factories yet in operation able to produce high-quality materials and their construction requires very large investments. Noordegraaf therefore recommends developing the technology for materials using first generation raw materials, such as sugar from sugar beets. Beet processing is a highly efficient activity that has been around in the Netherlands for a long time. This would lead to faster optimisation of the technology and, in turn, to faster commercial production. Production can then gradually switch to residual waste flows as raw material.
A consequence of the current policy, according to Noordegraaf, is that the Chinese are already building factories for the production of biobased materials even though the industrial sector in the Netherlands started conducting research and development several years earlier: 'We need to act quickly so as not to miss this opportunity. I feel rather pessimistic about the future of Dutch companies in this regard.'

Outstanding properties

Despite his criticisms regarding upscaling and commercialisation, Noordegraaf is positive about the research into new biobased materials being conducted as part of the BPM programme. 'Inventing is one of our strengths,' he explains. 'As part of BPM, companies and knowledge institutes have jointly developed various concepts for biobased materials with outstanding properties.' And the trend is a positive one. More and more large companies are investing in the research and development of biobased materials and green production processes. We must now switch to reaching out to consumers who are largely unaware of the wide range of applications for which biobased materials can be used. Weustink and Noordegraaf realise the importance of providing consumers with accurate information to make them aware of the many possibilities and advantages of biobased products. The Netherlands should not only focus on invention and production, Noordegraaf believes, but also innovate, by putting its inventions on the market. He believes biobased products should become attractive and appealing. He goes on to explain, 'The government's role is simple: it only has to facilitate the marketing activities and this can be done with no impact on the budget. What are we actually waiting for?'

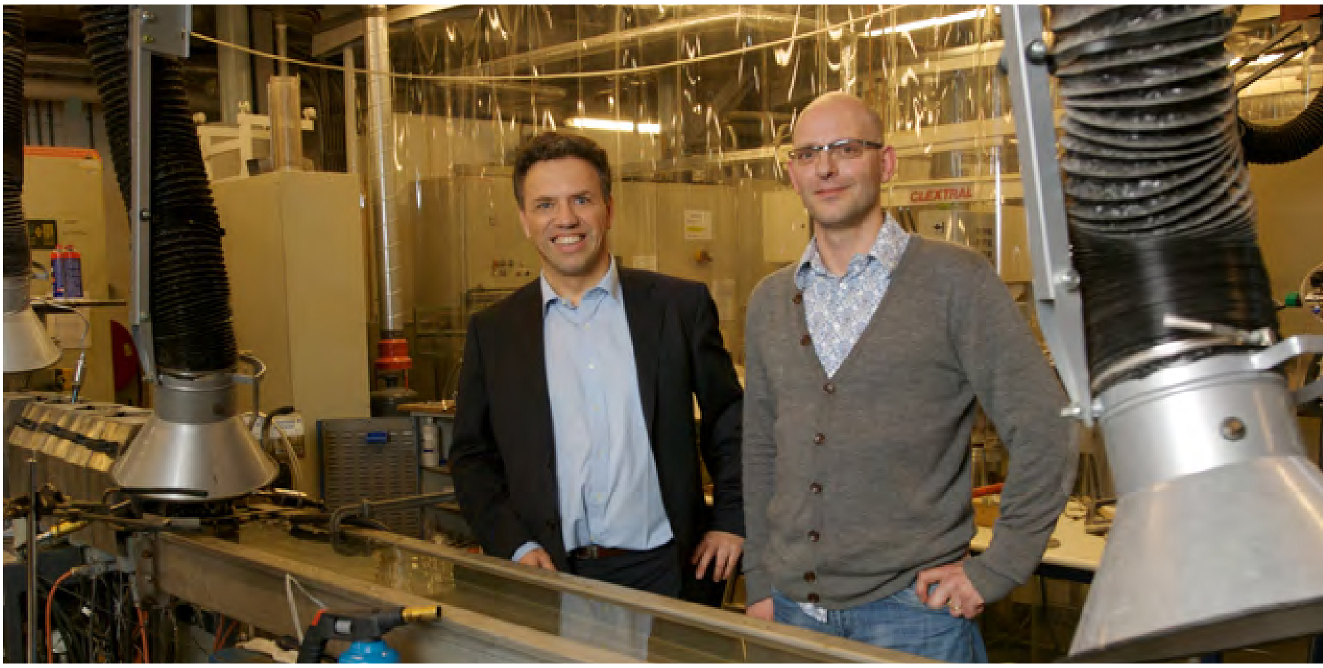
'As part of BPM, companies and knowledge institutes have jointly developed various concepts for biobased materials with outstanding properties'

New insights

Christiaan Bolck, director of the BPM programme, also looks back with satisfaction at the first five years of BPM. 'BPM is a success,' he says. 'The collaboration between the companies and knowledge institutes in most cases has been very successful, both in terms of research output and the way the research was organized. We now need to go for it one hundred per cent.' He believes BPM has so far already produced significant new insights into biobased materials. For example, researchers from knowledge institutes joined forces with researchers from industry to develop new biobased coatings, stronger PLA-based plastics and an economically feasible route for biobased methacrylate plastics. Due to these new materials and knowledge, companies started looking at wider, more robust applications of biobased materials: it can be used for so much more than just disposable packaging.

From building blocks to end product

The success of the BPM programme is due in part to its multidisciplinary character. The research focused on the entire production chain from the very start. Researchers and companies first decided which product they wanted to make from biobased materials by asking themselves which materials were in demand. They then switched their attention to the rest of the chain, questioning how to make the product



BPM project partners Hans Ridderikhoff (Croda) and Rutger Knoop (Food & Biobased Research)

with biobased materials and which biobased building blocks and raw materials would therefore be needed. The programme has already made a significant contribution to bringing together various scientific disciplines and companies from a range of different sectors. This is already a significant change in just a few years' time. 'Five years ago, many biobased-related research projects were still focused on sub areas, such as using biotechnology to create a biobased building block,' explains BPM Research Director Jacco van Haveren. 'The development of the product did not get any further in the value chain. Thanks to BPM, the focus has been extended to the entire chain: from building blocks to end product.' In addition, BPM also fulfilled a role that went much further than knowledge about new materials. As companies were actively involved in the research, researchers from both knowledge institutes and from industry shared their insights and experience, resulting in the transfer of a great deal of know-how. As Bolck explains, 'In this way, BPM also served as a platform for the exchange of knowledge between knowledge institutes and companies.'

Stimulating innovation

According to Bolck and Van Haveren, new projects should be set up along the same lines in future. It is also important to incorporate existing knowledge on materials and production processes when designing new biobased materials. 'We're not just talking about CO_2 reduction but also about economic aspects,' Van Haveren underlines. 'Not only is the bulk production of biobased materials important but also, or even more so, the production of specialty products on a relatively small scale but with a higher market value.' Considering the ambitions to develop the biobased

Thanks to BPM, the focus has been extended to the entire chain: from building blocks to end product'

economy, Bolck and Van Haveren believe that more money should be invested in the research and development of biobased performance materials that could compete, for example, with fossil plastics. Biobased ambitions can be found in government and company target figures, but achieving these figures does mean giving concrete form to these ambitions. 'In addition, policy should be organised more on the basis of a future vision rather on the current situation,' Bolck suggests. 'Within this context, we should be identifying and stimulating new top sectors such as the biobased economy rather than basing our activities on existing top sectors. However certainly we need existing industries from old sectors; but only those that continuously re-invent themselves. They are an essential pillar for the success of the ambitious

Transparent powder coatings and polyurethane coatings without toxic substances

After four years of research, two promising, environmentally-friendly coatings are now ready. Using their extensive knowledge of chemistry and materials, researchers and industrial partners collaborated within the NOPANIC project to develop both |widely-applicable coatings.

In search of a more environmentally-friendly version, researchers took a close look at polyamide powder coatings and waterborne polyurethane coatings. Both coatings consist of polymers with amide bonds (powder coatings) or urethane bonds (waterborne coatings) as a basis. 'For both coatings, we collaborated with our project partners to find a biobased version that could also be produced with greener chemistry,' explains Bart Noordover, university lecturer in Polymer Materials Chemistry at Eindhoven University of Technology.

Powder coating

Transparency of the material was an important criterion for the new biobased powder coating as it enables more effective colouring by the producer. The powder coating becomes hazy when the polyamide molecules start forming crystals; a phenomenon the researchers were looking to avoid.

'Crystals develop once the polymer chains are able to form a regular structure,' Noordover explains. 'We were able to prevent this regular arrangement of polymers by using asymmetrical building blocks of varying lengths developed by Food & Biobased Research. This produces an irregular chain structure that prevents crystal formation, keeping the material transparent.'

Powder shelf life

In the development of the new powder coating for project partners AkzoNobel and Nuplex, another important consideration was the shelf life of the powder at temperatures up to around fifty degrees Celsius. If the polyamide powder becomes hotter than fifty degrees, the fine powder particles can start to stick to one another. A bag of powder would then change into a rock hard, unusable mass. This risk is particularly prevalent with transparent polyamides with no crystal structure. These materials are often soft at relatively low temperatures: the polymer chains are flexible and mobile and more likely to adhere to one another. The researchers were able to prevent this from happening by incorporating isoidide diamine (a sugar-based molecule) into the polyamide chain. This made the chains stiff and less mobile. The powder then retains its powdery texture even at higher temperatures. In collaboration with Croda, Food & Biobased Research succeeded in optimising the synthesis of the isoidide diamine. 'Our successful collaboration with Croda enabled us to quickly scale up the process developed in Wageningen, so that sufficient resin-grade diamine was available for our partners,' says Daan van Es, senior researcher at Food & Biobased Research.

Toxic substances

The environmental benefits of a biobased version of waterborne polyurethane coatings were even greater than with powder coatings. When producing these coatings, producers use toxic substances, such as isocyanates and phosgene. The researchers came up with an alternative production process which no longer required these substances. 'We used glycerol as a basis. This is a cheap by-product of the bio-diesel industry and is mainly produced from vegetable oils,' explains Noordover. 'We used it to make so-called cyclic carbonates. These building blocks react together with amines to produce a polyurethane polymer without the need for toxic substances.'

Critical step

Recent tests conducted at the Eindhoven University of Technology and at participating companies have shown that the new biobased coating has good properties. 'We already have the basis,' explains Noordover. 'The next step is to produce the polymer on a larger scale so that the industry can conduct further tests for specific applications.' Noordover is convinced this will eventually happen, not only because of rising oil prices, but also because of increasing demand for cleaner, sustainable materials. In addition, EU and Dutch policies are focused on replacing toxic chemicals ('substances of very high concern') in the production process. Recent research conducted by Wageningen UR Food & Biobased Research at the request of the Netherlands National Institute for Public Health and the Environment (RIVM) underlined the availability in many cases of good biobased alternatives. Noordover explains, 'It would be fantastic if we could make a contribution with our research to a cleaner production process.'

Polyhydroxyurethane with Tg-value above room temperature (left) and around room temperature (right)

PROJECT PARTNERS

AkzoNobel
Croda
Wageningen UR Food & Biobased Research
Nuplex
Eindhoven University of Technology
Utrecht University
Ursa Paint

Incorporating flexible building blocks for tough PLA

As part of the HIPLA project, the collaborating research partners have developed a new biobased plastic that has a higher impact resistance than traditional polylactic acid (PLA). As a result, this PLA can be used for a broader range of applications, such as in high-quality plastic housings for laptops and tablets.

The aim of the study was to improve the biobased plastic polylactic acid, PLA for short, that was already commercially available. This bioplastic consists of linked lactic acid molecules, polymers, which are based on sugar. To make PLA tougher, the project team was able to draw on the experience they had gained from working on other materials. Incorporating a natural, flexible building block into the brittle plastic turned out to be a success.

Flexible building blocks

In an earlier study, Croda Nederland BV in Gouda was able to considerably strengthen a hard but brittle epoxy coating by adding fatty acid particles. The new coating was just as hard but its increased flexibility meant it did not break as easily. 'The main question was whether this principle would also work for PLA,' says Angela Smits of Croda Nederland. 'One of the biggest challenges was incorporating this flexible building block into the PLA polymer. After all, it is a very different material than an epoxy coating.'

Ultra-tough bioplastic

By specifically experimenting with heat and friction in the polymerisation process, the researchers finally succeeded in building the biobased fatty acid molecule into the PLA polymer chain. 'Since these fatty particles cluster together in the PLA polymer matrix, they look like spheres under the microscope,' Smits explains. 'In the hard PLA matrix, these built-in spheres now ensure the material is impact-resistant.' And the result is impressive: an ultra-tough bioplastic that can be used for a wide range of applications.

Film coatings

This new basic material was used by AFP, a film manufacturer in Apeldoorn, to produce a film on a pilot scale. Smits thinks this new material could be used as packaging material that does not crack, as well as for film coatings for car dashboards and films that can be used in greenhouses. HSV Technical Moulded Parts in Ede successfully tested the material as a raw material for plastic components by injecting or pouring the melted mixture into larger moulds. HSV also successfully tested the material in an application as printer panel. 'We are making good progress, but still need to make technical improvements and optimise costs before it can be used in mass production,' says Smits. 'The patent is being processed and in follow-up research we would like to apply these principles to other biobased plastics.'

PROJECT PARTNERS

AFP
Croda
Wageningen UR Food & Biobased Research
HSV
Synbra

STRETCHING PLA

PLA properties improved through stretching and crystallisation

By making clever use of the specific crystallisation behaviour of polylactic acid (PLA), it has proved possible to produce a PLA bottle that is both almost transparent and tough, but which hardly, if at all, loses its shape at temperatures up to 90 °C.

PLA is a versatile, 100% bio-based and bio-compostable plastic that is already used in a wide range of products. PLA could be used for an even greater number of applications if properties such as toughness, maximum service temperature, and barrier characteristics are improved. As part of the PLA-StIC project, researchers from Eindhoven University of Technology and Wageningen UR Food & Biobased Research joined forces with seven industrial partners from the entire production chain (from raw material supplier to end-user application) to try and improve these properties by taking advantage of PLA's specific crystallisation behaviour during processing. A decision was made to demonstrate the results of the project through the production of bottles; the principles found can also be applied to the production of fibres, films, thermoformed products and foams.

Crystal formation during stretching

'PLA crystallises relatively slowly and most PLA products currently on the market are hardly crystalline, if at all,' explains Gerald Schennink, researcher at Wageningen UR Food & Biobased Research. A well-known example is the PLA cup currently used at major festivals which are amorphous rather than crystalline and therefore only suitable for cold drinks. 'And yet it is not difficult to make crystalline and semi-crystalline PLA cups which are also suitable for holding hot drinks,' Schennink says. This involves, among other things, taking advantage of the orientation and stretching processes that occur during the manufacturing of these products.

Purity of PLA determines crystalline behaviour

'It is important to tune the choice of raw material and the process parameters,' Schennink explains. When making a PLA product, it is important to know whether the polymer is synthesized from only left-rotating or right-rotating lactic acid, or both monomers are used to form what is known as a copolymer. If a polymer consisting purely of left-rotating lactic acid (PDLA) is added as an additive to a PLA polymer or copolymer with little or no left-rotating lactic acid, a type of crystal (stereocomplex) develops during processing which not only has a higher melting point but also accelerates the entire crystallisation. This mechanism was applied during the research.

Thermostable and transparent PLA bottles

The study shows that it is possible to produce a PLA bottle that is transparent and tough, and which hardly, if at all, loses its shape at temperatures up to 90 °C. However, the bottle is not yet suitable for carbonated drinks. 'Carbon dioxide leaks through the bottle wall,' explains Pim Lohmeijer, researcher at the Laboratory of Polymer Materials of the Eindhoven University of Technology. 'Although the formed crystals may improve the bottle's barrier properties, the blow moulding process stretches the material to such an extent that minuscule voids develop.' It may be possible to prevent the formation of these voids by studying the conditions of the stretching process more closely.

Model provides greater insight

To better understand the relationship between stretching conditions, crystallisation behaviour and the properties of the final product, Lohmeijer and Schennink tried to create a model which captures the various processes that occur during stretching. Researchers at Eindhoven University of Technology concentrated on the in-line study of the crystallisation behaviour during 1D stretching of PLA tapes. Researchers at Food & Biobased Research focused on performing 2D stretch tests of films and sheets, and ultimately the production of bottles. The combined research yielded information relating to raw material choice, crystal formation and the final properties of stretched, crystalline PLA products. Finally, the research team discovered that not only crystallinity, but also orientation of the non-crystallised material is important for the final properties of a PLA product. This knowledge can be used, for example, in the production of shrink films.

PROJECT PARTNERS

Constar
Croda
Desch Plantpak
Wageningen UR Food & Biobased Research
FKuR
Corbion Purac
RedOrange Food
Synbra
Eindhoven University of Technology

Cost-effective production of biobased bulk chemicals

Citric acid is a very inexpensive and renewable raw material, nowadays used as a food additive. It can also be effectively converted into methacrylate, as discovered by researchers participating in the ACTION project. Methacrylate-based polymers have exceptional optical properties and can be used for a wide range of applications, from plexiglas, coatings and glues to optical conductive fibres.

BPM's ACTION project focuses primarily on finding biobased building blocks for the production of industrial bulk chemicals. 'It is not usually the chemistry is the limiting factor as biomass can be used to create almost anything,' explains project leader Jacco van Haveren. 'It is still mainly about minimizing production costs that currently determine whether a biobased variant would be of interest to industry.'

ICT sector

Most of the development work on biobased materials currently focuses on the use of polymers obtained by means of polycondensation chemistry. A well-known example of this is polylactic acid. However, many of the traditional plastics are based on polymers obtained through radical polymerisation. Alongside ethylene and propylene, important building blocks for these types of polymers are styrene, acrylic acid and methacrylic acid. To make such products more biobased, the project was initially based on a concept in which two of the building blocks could be made from biobased raw materials at the same time: styrene and acrylic acid from amino acids and acrylic acid and methacrylic acid from itaconic acid. Although this concept was successful on a lab scale for the coproduction of styrene and acrylic acid, due to the high production costs involved, the manufacturing industry was not interested in scaling up. The research team subsequently decided to focus its research on the development of a biobased methacrylate. This widely-applicable raw material is related to acrylic acid, but PMMA polymer based on methacrylate has the exceptional optical property of being extremely transparent. One particularly interesting application of this material is in optical conductive fibres. These can replace copper-based electrical cables, such as those used for computers, thus making the ICT sector more sustainable.

Limiting costs

After a thorough literature search, Van Haveren discovered a publication in which the authors explained how methacrylate could be produced from citric acid in supercritical water at 370 degrees. This production process was optimised by the research team who used a catalyst to enable the reaction to occur at lower temperatures and much more efficiently. This new process gave the team a relatively simple and efficient method for converting citric acid into methacrylate. It also provided cost benefits. Methacrylate costs around two thousand euros per tonne, while citric acid costs only five hundred euros per tonne. 'This provides quite a considerable amount of financial leeway,' says Van Haveren. 'We can also reduce costs even further by producing citric acid from cheaper raw materials.'

'It is mainly due to the efficiency and low costs of our process that it opens up very real opportunities for the manufacturing industry,' explains Van Haveren. 'We are therefore seeking companies that would be interested in further optimising the process and facilitating bulk production.'

PROJECT PARTNERS

BASF
DSM
Wageningen UR Food & Biobased Research
GreenICT
Synbra
Wageningen University

FILM BASED ON CHITOSAN

Chitosan coating gives film antimicrobial properties

Important steps have recently been taken in the development of an antibacterial packaging film based on chitin for use in products such as stand-up pouches for Heinz soup. 'We now have a result we can work with,' says Eddy Hilbrink, Strategic Product Developer at AFP, a film manufacturer based in Apeldoorn.

Chitin is a substance found in the exoskeletons of insects and crustaceans, as well as in some fungi. After being converted into chitosan and subsequently the monosugar glucosamine, it can be used as a dietary supplement. Chitin and chitosan have both antimicrobial properties. Wageningen UR Food & Biobased Research has developed technologies, e.g. using enzymes, to convert chitin into chitosan using less or no aggressive chemicals.

Testbatch foil and granules based on chitin

Challenges

In developing an antimicrobial film containing chitosan, the researchers of the ChitoSmart project were faced with some considerable challenges from the very start. 'Mixing the antimicrobial chitosan into the plastic film continued to cause problems,' explains Hilbrink. 'It was impossible to distribute this substance homogeneously. It remained lumpy in the film, possibly causing it to lose its antibacterial effect.' The chitosan also appeared to adversely affect the film, causing a yellowish discolouration after the substance had been mixed in.

Breakthrough

The research team – consisting of members from AFP, Wageningen UR, Heinz and TNO – decided to try a different approach: instead of mixing the chitosan into the plastic film, they developed a coating made from chitosan which was applied to the film. However, a disadvantage of this method is that it requires an additional step, making the process more expensive. Despite these drawbacks, the project recently achieved a notable success, as evident from tests of special methods developed as part of the project. Frank Schuren, microbiologist and TNO researcher, explains: 'Our most recent series of tests shows that AFP's latest coated film has antimicrobial properties. This is an important breakthrough in the development of a plastic packaging which can be used to keep food shelflife longer.'

Cost-effective

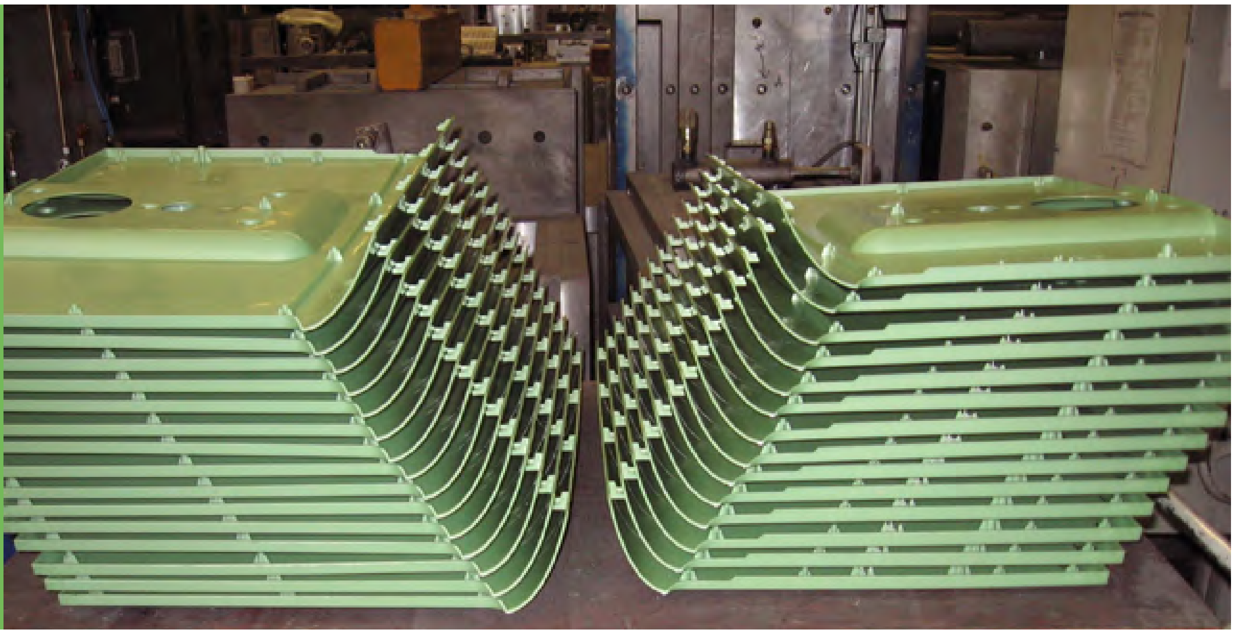
Although the foundation has been laid, the coating, according to Hilbrink, is not yet ready for the supermarket. Its suitability still needs to be proven in practical trials. 'We first need to carefully examine the adhesion of the coating on the film,' he explains. 'In addition, we still don't know how the coating affects the sealing of the film.' The tests must also demonstrate whether the antibacterial properties are just as effective in practice as during the TNO tests.

Broader range of applications

The initial success with the coated antibacterial film makes the researchers optimistic. However, Hilbrink thinks that a film into which chitosan has been mixed will turn out to be cheaper and suitable for a broader range of applications than a coated version. A coating that is applied to a flexible film can easily tear. This is less likely to happen if chitosan is mixed into the film. Tearing seems to be less of a problem if the coating is applied to less flexible products, such as plastic bottles. 'Much still needs to be developed in terms of both coated and non-coated antibacterial films and we are eager to continue our research,' says Hilbrink resolutely.

PROJECT PARTNERS

AFP
Wageningen UR Food & Biobased Research
Heinz
Nippon Suisan
TNO



Suitable biobased plastics for printer panels

Within the FEASIBLE-project raw material suppliers, processors and end-users were supported by researchers on their search for alternatives to oil-based plastics. 'We were specifically looking for commercially available biobased materials that are suitable as a replacement for commonly-used oil-based plastics in demanding applications,' explains Karin Molenveld, researcher at Wageningen UR Food & Biobased Research. The researchers studied alternatives for barrier packaging, carpet backings and electronic housing. Manufacturer Océ, for instance, was interested in a biobased housing for printers.

The development of many biobased materials for industrial applications is still in its infancy, but that is only logical. It took fifty years for oil-based plastics to develop into the current generation of high-quality plastics. According to Menno Krommenhoek, Business Unit Director at HSV Technical Moulded Parts BV in Ede, it was a real challenge to find suitable biobased alternatives. 'The bar was set very high,' he says. 'It's quite a task to find biobased alternatives that are fire-retardant, heat-resistant and have sufficient strength.' More research and development is still needed. At the same time, there needs to be more focus on market development. And the market for plastics is developing quickly. There is a clear trend to replace more and more materials, such as metals and ceramic, with plastics. As Krommenhoek explains, 'The switch to biobased plastics is an important one but cannot be made in one go.'

Thorough testing

The FEASIBLE project team tested around twenty different biobased plastics. The researchers used standardised methods to test relevant properties such as strength, fire-resistance and maximum usage temperature. In addition, HSV tested the processing of various materials into printer panels by means of an injection-moulding process. Test samples were then cut from large printer panels to undergo further testing in the laboratory. 'Since test methods and specifications can differ considerably for materials from different manufacturers, it is important that we selected and conducted these tests ourselves,' Molenveld explains. 'This is the only way to ensure a fair comparison of the materials.' Various tests indicated that hybrid plastics – plastics consisting of a mixture of oil-based plastics and renewable materials (such as PLA) – were closest to achieving the properties we were looking for.

Knowledge of hybrid plastics

Krommenhoek and Molenveld believe that the extensive knowledge gained on available hybrid plastics and their possible applications is an important result of the FEASIBLE project. All this knowledge has been compiled into lists of various materials and their properties. As Molenveld explains: 'End-users can use the lists to find the properties they are looking for and then select the material most suitable to their requirements.' According to Krommenhoek, there is now substantial information about the current situation and the benefits and drawbacks of biobased plastics. Hybrid plastics are suitable for use as standard plastics (such as polystyrene or polypropylene) but they have the price of an engineering plastic (such as polycarbonate blends). As Krommenhoek explains, 'You can accomplish quite a lot with certain materials. If the industry wishes to promote a green image and is prepared to pay the extra costs, either temporarily or permanently, interesting opportunities open up.' And it seems like the industry is highly motivated to develop improved biobased plastics. During the first injection moulding trials, one of the hybrid material based on PLA and polycarbonate did not show sufficient flow .
Two weeks later, the company sent a new mixture that die fulfill expectations. As Molenveld explains, 'The research apparently encouraged the producer to develop a new materials. This type of effort is invaluable!'

PROJECT PARTNERS

Ahold
Croda
Wageningen UR Food & Biobased Research
Heinz
HSV
Jus de Pommes
NatureWorks
Océ
Corbion Purac
Rinos
Rodenburg
Synbra
Utrecht University

Dimer fatty acids improve PBT

As part of the MOBIOSOL project, researchers developed not only new powder coatings but also a new industrial plastic based on the widely-used polybutylene terephthalate. The new material is partly made from biobased building blocks and is tougher and more versatile than traditional PBT.

The electronics and automotive industries make considerable use of industrial plastics such as PBT, a plastic that is related to the more widely-known PET. These substances meet stringent requirements. They are strong, can withstand impact, and are also heat-resistant. PBT is mainly used in industry for high-precision components in cars and electronic equipment. The material does a good job but does have several drawbacks. The plastic is somewhat brittle and it is based on crude oil. The MOBIOSOL researchers focused, among other things, on making PBT greener and tougher by using alternative biobased building blocks.

Brittleness

PBT is made from two fossil feedstock-based building blocks (butanediol and terephthalic acid). Together, these form a long polymer chain. Some of the polymers are crystallised and are embedded as small crystalline domains in a non-crystallised, or amorphous, region. This amorphous matrix is brittle below forty degrees Centigrade but the crystallised areas add rigidity to the material. Above forty degrees, the matrix becomes tougher and more rubbery. The researchers wanted to develop a new, partly biobased, plastic based on PBT that becomes tough at room temperature. However, incorporating a biobased building block following conventional chemical methods has a negative effect on the crystal clusters, leaving fewer and smaller crystalline areas behind. ‘As a result, the melting point drops,’ explains Cor Koning, Science Manager at DSM in Zwolle. ‘This, in turn, leads to a lower service temperature, which means the material is far less versatile.’

New method

A special production process, developed by Eindhoven University of Technology, resulted in the best of both worlds: a strong industrial plastic based on partly biobased raw materials that can be used for a wide range of applications. In collaboration with Food & Biobased Research, Croda BV from Gouda developed and produced fatty-acid biobased building blocks for this purpose. 'This collaboration makes efficient use of one another's expertise and facilities to create dimer fatty acids that are pure enough to build into polymers,' explains Daan van Es, senior researcher at Food & Biobased Research. 'With this new method, we succeeded in incorporating the fatty-acid building block into the amorphous part of the PBT only,' says Bart Noordover, university lecturer in Polymer Materials Chemistry at Eindhoven University of Technology. 'As the building block is only built into the polymers in the amorphous part of the PBT, the PBT crystals remain unchanged.' The result is a less brittle, tough plastic that is strong and able to withstand high temperatures.

Modified production method

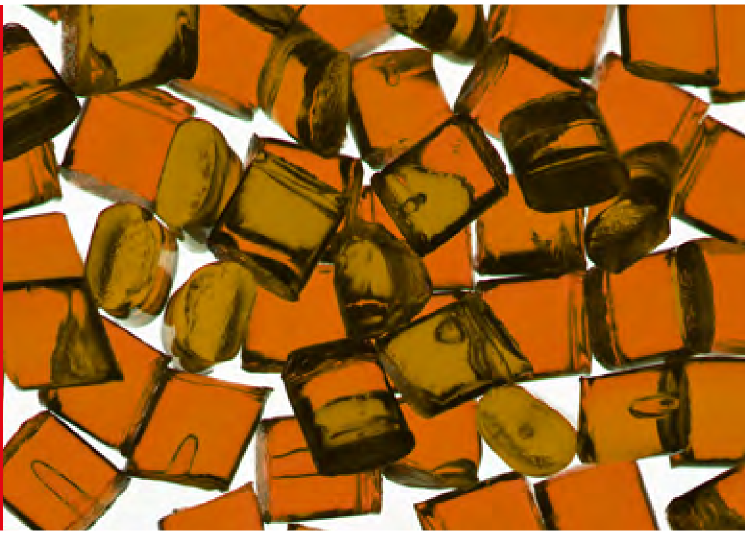
'MOBIOSOL has produced an extremely interesting biobased industrial plastic,' Koning confirms. 'The special production process leaves the crystallised areas intact, not only ensuring sturdiness, but also a melting point that is no less than twenty degrees higher than in a conventional production process.' This enables the material to be used for applications in which it will become hot, such as in the automotive and electronics industries. There are, however, drawbacks to the method used. The costs of the fatty-acid building blocks are still high, for example, and the new method also requires a large amount of solvent. 'We therefore need to look for a modified production method, without the need for solvent, if we want to produce this plastic on an industrial scale,' Koning suggests.

PROJECT PARTNERS

Avantium
Croda
DSM
Wageningen UR Food & Biobased Research
Eindhoven University of Technology

COMPOSITE RESINS

Composite resins based on isosorbide and recyclable variant



Researchers working on the BIOCRES project have developed two different biobased composite resins. The products made from these new resins are just as strong as those made from traditional polyester resins but the building blocks are made from renewable raw materials and are also less toxic. One of the resins is also reusable. These are extraordinary results for a thermoset resin.

Thermoset composites have become an indispensable part of modern society. These two-component plastics - consisting of a resin and a fibre - are lightweight, strong and heat-resistant. This makes them suitable for a wide range of applications and they are often used in the automotive and aircraft industries. In the production of composite resins, individual building blocks are joined together to create a resin consisting of long chains called polymers. The resin is dissolved in styrene immediately after production to form a liquid mass. Composite products are created by pouring the resin formulation into a mould of the required shape, in which fibre mats have been placed to reinforce the end product. During treatment with heat, the styrene reacts with the resin, cross-linking the polymers to create a strong network. This changes the liquid resin into a hard, sturdy plastic.

Greener alternative

Conventional polyester composite resins are, however, not environmentally-friendly. The polymer chains are constructed from crude oil components and are difficult to recycle. Furthermore, toxic styrene is needed to cross-link the individual polymers together into a network. As a result, the resin can contain thirty to forty per cent of this toxic substance. Researchers believed it was time for a greener alternative: a composite resin based on biobased building blocks that would preferably also be fully recyclable.

Similar properties

Wageningen UR Food & Biobased Research developed a resin based on furandicarboxylic acid. In addition, researchers also succeeded in creating a biobased substitute for styrene. 'The combination of isosorbide diallyl ether and isosorbide dimethyl acrylate produces properties and applications similar to those of the conventional composite material, but roughly two thirds of the combination consists of biobased components based on sugar,' explains Rolf Blaauw, researcher at Food & Biobased Research (FBR).

Fully recyclable

Francesco Picchioni, a professor of Chemical Product Engineering at the University of Groningen, also believes in the reuse of composite resins. 'Going green is not enough: environmental gains are limited when only green building blocks are used,' he explains. At the same time as FBR, Picchioni's team developed a different resin, with greater emphasis on recycling. The team developed a new resin composed of a biobased version of bisphenol A and terephthalic acid. No longer does the resin need to be dissolved in styrene, but becomes liquid when heated, after which it can be processed. However, this bisphenol A variant could pose a health risk for resin producers who become exposed to it during the production process. In addition to the new polymer, the team in Groningen also developed an alternative to the cross-linker styrene: a bismaleimide. Less toxic than styrene, it does however do the same job of cross-linking the polymer chains together. This new resin is now fully recyclable, representing a breakthrough in the research conducted in Groningen. 'By simply heating the resin to approximately 140 degrees Celsius, the network structure disappears,' explains Picchioni. 'This returns exactly the same individual polymers again, fully in keeping with the cradle to cradle principle.'

Combining inventions

It seems obvious to the researchers in Wageningen and Groningen to combine their inventions to create a non-toxic, recyclable resin. However, this does require a significant technical step. 'We could combine the non-toxic resin developed in Wageningen with the bismaleimide cross-linker and the chemistry developed in Groningen,' Blaauw suggests. Picchioni also sees ample opportunities for combining the best of both products. 'It would certainly be possible to apply the concept of degradable and recyclable network structures to the resin made in Wageningen,' he says. 'All we need now is an interested business partner.'

Project partners

Cargill
Cosun
Wageningen UR Food & Biobased Research
NPSP Composites
Nuplex
University of Groningen

Analyzing the environmental benefits of developed biobased materials

Biobased materials have developed from single-use disposable packaging to high-quality plastics for industrial applications. According to researchers taking part in the SUSTAIN project, despite the environmental benefits of renewable raw materials, significant improvements can still be made in production

How environmentally-friendly is the production of biobased materials nowadays compared to petrochemical products? This question was raised by Li Shen, senior researcher at Copernicus Institute, Utrecht University, Group Energy & Resources. Shen was closely involved in the SUSTAIN project, in which early-stage sustainability assessment was carried out for the products developed by the other BPM programmes. The assessment focussed on energy and GHG emissions for the entire production chain of the developed biobased performance materials.

The environmental impacts were compared to the petrochemical counterparts. Based on the findings of SUSTAIN, recommendations were made for raw material selection and for the improvements in the production process. 'It is hard to draw a general conclusion that applies to all biobased materials,' Shen says. 'The picture is not black and white. However, some biobased materials do show very promising potential impact reduction, such as methacrylate produced from citric acid.'

Environmental impact

In SUSTAIN, the method of ex-ante life cycle assessment (LCA) was applied for the environmental assessment. By using this method, the environmental impacts were analysed for the so-called "cradle-to-factory gate" life cycle of a product. Lab data was collected for the analysis from various BPM subprojects. 'In an LCA we analyse the environmental impacts of each step in the product's life cycle,' Shen explains. 'This includes the extraction of natural resources, such as oil drilling, as well as transportation and all the steps in the final production process.' Based on this type of analysis, she was able to give advice on the choice of raw materials for making biobased materials and also to make an objective comparison with petrochemical products. It was found, for example, in the production of biobased polyurethane (NOPANIC) that the conversion of di-glycerol into cyclic carbonates is highly efficient due to high yield, less waste and the innovative catalytic conversion which requires mild reaction conditions. However, for the biobased polyamide developed by NOPANIC, Shen believes there is room for improvement in the production of several raw materials (e.g. benzyl amine) as it requires a relatively large amount of process energy.

Considerable challenge

Although biobased materials could provide significant environmental benefits compared to their petrochemical counterparts, this picture is not as black and white as it seems. Even though biobased raw materials are often considered 'green' because they are made from plants and are thus renewable, the amount of energy used during the production process could still be significantly higher than that for petrochemical products. This is no more than logical. Biobased production processes are still in their infancy and therefore not yet optimum. According to Shen, this represents a challenge for certain materials. Significant progress can still be made in the production of biobased polyamides, for example, which currently require considerably more energy to produce than their petrochemical counterpart. 'The large amount of energy needed means the process energy consumption will have to be reduced considerably or researchers will need to consider a completely new chemical synthesis route,' Shen advises.

Energy savings

Despite the challenges still faced, the production of biobased materials is becoming increasingly efficient and great progress has been made in that respect over the last decade. Substantial improvements have been made in the production of PLA, for example. PLA producers have been able to reduce the amount of energy needed to process the raw material – and also improve the fermentation process. As a result of this optimisation, far less energy is needed and CO_2 emissions are much lower. Significant improvements can also be made for other materials, such as biobased styrene. Reductions must be made, according to the researcher, in the amount of energy, solvents and reactive substances used in the production process. This may sometimes entail taking a completely new approach, as was the case during the production of biobased polystyrene (ACTION project). 'Researchers first produced this substance from amino acids, but this cost too much energy,' Shen explains. 'A completely new production method based on citric acid instead of amino acids proved to be much more energy-efficient.' Despite these challenges, a more efficient production of biobased materials is, according to the researcher, simply a matter of time. As Shen explains, 'Biobased materials are definitely part of our future as we find it necessary in the long term to replace traditional products due to dwindling oil supplies. This means there will be increasing demand for biobased products.'

The central point for knowledge and expertise on biobased materials in the Netherlands

Research in public private partnerships in the Netherlands is organized in business sectors. Within these so called 'Topsectors', the BPM programme coordinates research and development in the field of biobased materials. As such it brings together both knowledge and researchers in the field. BPM is currently already performing this task for the top sectors of Chemistry and Agri & Food, but the programme is also important for the top sectors of Energy, Horticulture & Propagating Materials, High-tech Systems & Materials, and Water.

The ambition of the BPM programme is to develop biobased materials that - in terms of material properties and price - can at least compete with their petrochemical counterparts that are currently used to make toys, computers, mobile telephones, household appliances, cars and as components in paints, coatings, carpets and sheeting materials.

Following a value chain approach, within the core programme of BPM, applied research institutions and universities from the Netherlands work together with companies from within and outside the Netherlands. Support is also provided to regions, and BPM links up with European initiatives. On top of that BPM organises valorisation activities for SMEs, as well as education activities.

BPM is therefore the central coordination point for knowledge and expertise on biobased materials in the Netherlands.

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