GREEN POLYMERS

With special attention to the differences between

BIO-BASED

BIODEGRADABLE

RECYCLABLE

COMPOSTABLE (industrial - home)

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CENTEXBEL-VKC

GENT | Technologiepark 70 | BE-9052 Gent | Belgium | +32(0)9 220 41 51 | gent@centexbel.be
KORTRIJK | E. Sabbelaan 49 | BE-8500 Kortrijk | Belgium | +32(0)56 29 27 00 | info@vkc.be
GRÂCE-HOLLOGNE | Rue du Travail 5 | BE-4460 Grâce-Hollogne | Belgium | +32(0)4 296 82 00 | g-h@centexbel.be

www.centexbel.be

Biodegradable products

Centexbel tests expose facts and fiction

Brecht Demedts | Brigitte Bossuyt | Myriam Vanneste

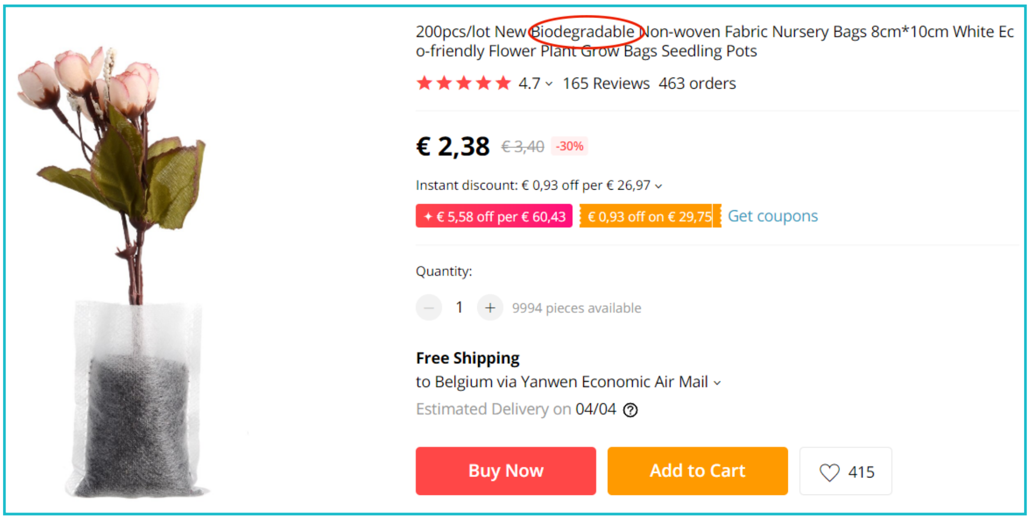
The booming market of biodegradable products has a beneficial effect to the environment. However, not every product that is sold as being biodegradable really is biodegradable, for some marketeers are seizing this lucrative opportunity to mislead their often-gullible customers. As customers are becoming increasingly aware of the environment, they tend to prefer buying a product that is labelled as biodegradable to one that is not. This trend explains the steep increases in the demand for biopolymers and development of ecological products. But can we take all bio-claims at face value?

Centexbel test results revealed that none of the items bought on the Chinese webstore AliExpress was biodegradable, although they are being advertized as such!

Biodegradable products put to the test

Because "the proof of the pudding is in the eating", we randomly purchased several biodegradable products in local grocery stores as well as online at AliExpress for further analyses. Centexbel has a very thorough and longstanding expertise in the assessment and characterization of textiles, polymers and plastics, which is vital for this case study. The purchased samples have been submitted to infrared spectroscopy to identify the kind of plastics a material is made from. The results were mind-boggling!

None of the "biodegradable" plastics we bought on AliExpress proved to be biodegradable. The dog poo bags, plant seedling bags and horticultural trays were all made from polyethylene, the toothbrush was made from PBT and a nursery bag for plants was made from PET. Even though none of these polymers is biodegradable, it was explicitly stated as such on the Chinese webstore.



We also went shopping for biodegradable products in local stores in Belgium, where we bought biodegradable coffee capsules, wet wipes, sponges and grocery bags. Testing proved that all these products are indeed biodegradable. But this isn't the end of the story.

What does the biodegradability really mean?

The information provided on products can sometimes be confusing or even misleading. Therefore, a good understanding of the different terms and what they stand for is essential to guarantee the effect of the way we discard our waste.

Biodegradabilty:

In the presence of oxygen, at ambient temperature and under the influence of micro-organisms, a biodegradable material breaks down into CO_2, water, mineral salts and biomass.

In the absence of oxygen, the biodegradable material is converted into CO_2, methane, mineral salts and biomass.

Disintegration:

Degradation at a visual level. The item disintegrates into small pieces. Sometimes it breaks down into very small pieces that are no longer perceptible to the naked eye. For example: microplastics.

Composting:

A specialized form of biodegradation in which the product is broken down by microorganisms into a nutrient-rich substrate. This is subject to strict requirements in terms of process duration and compost quality.

https://www.tuv-at.be/green-marks/certifications/ok-compost-seedling/

Standards

Compostable plastics are defined according to standards EN13432, EN14995 or ISO17088 and must comply with the following principles:

- min. 90% biodegradation to water, CO_2 and minerals within 6 months; for home composting within 12 months
- low concentration of heavy metals
- no influence on the quality of the compost
- Because of the strong differences a distinction is made between industrial composting and home composting.

Downloads

List of standards on biodegradability

List of standards on biopolymers

“Compostable” doesn’t always mean biodegradable at home

There are different levels of biodegradability. Some items biodegrade at home, in your own compost pile, while others will only biodegrade in industrial composting processes, at 60°C with high humidity. Please note that many home compostable items do not biodegrade in cold seawater (certification for marine biodegradation see page 13).

For example, coffee capsules are made from a blend of PLA (polylactic acid = bio-based) and PBS (polybutylene succinate = not bio-based). In such cases it is important to clearly inform the customer that these cups are indeed biodegradable, but not necessarily home compostable. In the case of the coffee capsules, the statements on the packaging are theoretically correct, but might be deceiving.

The “100% bio compost” claim on the packaging probably refers to industrial composting, which is usually the case for PLA. It means that is is compostable under industrial conditions (heat and humidity) and that it will not biodegrade in your compost pile at home. However, it is not a certified label, and it is highly unclear in which environment these cups will actually degrade.

The “100% BIO COMPOST” on the package is a self-made claim and NOT A CERTIFIED LABEL, from which it is unclear whether the product is actually home compostible, which it is likely not, as PLA requires industrial composting at elevated temperatures.

“Biodegradable” and “bio-based”: two different concepts

The typical foil wrapped around magazines is made of thermoplastic starch, which is home-compostable, but not 100% bio-based. The starch is blended with special types of polyester or polycaprolactone, which are biodegradable materials, but not bio-based. Also note that the label states “foil 100% biodegradable”, which does not imply the printing ink. When analyzing the ink, we found it was polyurethane-based and therefore not biodegradable.

This plastic foil for wrapping up magazines and printed matter is properly certified as home compostable; it is however not 100% bio-based. The foil itself is indeed biodegradable, but the printing ink is not.

Why an identical bio-based wall paint happens to be a little more bio-based in the Netherlands?

Bio-based content is determined by means of the carbon 14 method specified e.g. in the American ASTM D6866 and the international ISO 16620 standards. With this method the age of the carbon in the product is determined. Most certificates require that 90% of the carbon in a bio-based product is younger than 10 years. Although both standards use carbon dating, the calculation of the bio-based content is different. According to the ASTM standard, all fillers (such as chalk) are removed from the calculation, whereas this is not the case in the ISO standard. The result is that a paint containing a lot of chalk gets a higher bio-based content by using the ASTM standard than when the same determination is done based on the ISO standard. And while the Dutch Directorate-General for Public Works and Water Management recommends the use of the ASTM standard, the ISO standard is almost always used by German labels.

And that is why the same wall paint in the Netherlands has a higher bio-based content than in its neighbouring countries.

Comparing biodegradation to incineration

One could reasonably argue that biodegradation is no different than just burning the trash. In the end, both result in CO_2 emissions. In general, the “Reuse, Reduce, Recycle” principle should be followed. In certain cases, biodegradation is strongly preferred, especially for those products that are meant to be used in the soil, such as agrotextiles, mulching films, and flowerpots or bags.

Obviously, items that are likely to be accidentally released into nature are preferably biodegradable. These products include for example wet wipes, that are too often non-biodegradable and flushed through the toilet, clogging our sewer systems. Where food packaging is too polluted with food to be properly recycled, a biodegradable packaging may be preferred. Biodegradation may however never be an excuse for littering.

This product provides the correct information. The wet wipes themselves are compostable, and the packaging is recyclable.

The Belgian law does not allow any plastics to be discarded together with the organic waste fraction, not even compostable plastics!

Most countries in Europe don't allow home compostable plastics to be mingled with the organic waste fraction, partly because of the confusion due to the many existing certifications on composting.

Let's take a closer look at a PLA-coated paper cup. The certificate states it is "compostable". However it is not home compostable. Therefore, this cup can neither be discarded into the organic waste fraction or recycled and will have to be incinerated after use. It certainly doesn't mean this PLA coated paper cup is bad, as less CO_2 is needed to produce such cup compared to a similar one in PE-coated paper. Nonetheless, it proves that some of the many certificates printed on these cups are misleading.

These coffee cups are labelled "compostable" and "no waste, better taste", but they are in fact not recyclable, not allowed to be discarded together with organic waste and therefore not home compostable. After use, they must be thrown away together with the combustible trash.

Centexbel is a pioneer in the research for bio-based and biodegradable materials

Few research centers started as early as Centexbel-VKC with the development of bio-based products. Centexbel is also successful in guiding companies in the challenging task of developing bio-based products. We currently see an interesting evolution in the development of bio-based materials. Whereas research used to focus on bulk material, more and more attention is now being given to the details, including printing inks, coatings and additives. This indicates that bio-based materials are maturing.

Centexbel-VKC is glad to support the industry with initiatives in bio-based and/or biodegradable items. Twice a year, we organize a training session, called 'Introduction to bio-based polymers' - https://www.centexbel.be/en/agenda

We have recently launched a new research project, called "Biocoat" to optimize and demonstrate the bio-based coatings developed in previous projects for all kinds of materials. Biocoat is a collective project, supported by VLAIO and coordinated by Sirris. Participation to the project is free of charge.

For more information & advice, contact Brecht Demedts | bdm@centexbel.be and Karim El Kassmi | kek@vkc.be

BIOCOAT project: https://www.centexbel.be/en/projects/biocoat

BIOGEARS is a new European Maritime and Fisheries Fund (EMFF) funded project that focuses on creating bio-based ropes, as an alternative to the currently used 100% non-recyclable plastic rope products, for use in offshore aquaculture. **BIOGEARS** uses an **Integrated Multi-Trophic Aquaculture (IMTA)**[1] approach by integrating seaweed and mussel production in order to increase marketable aquaculture products.

The current use of bio-based plastics - from biomass renewable resources and biodegradable in different environmental conditions - merely represents some one percent of the annual production of 335 million tonnes of plastics.

BIOGEARS will develop **durable and fit-for-purpose bio-based ropes** that are nonetheless **biodegradable** within a shorter timeframe and that can be **sustainably managed by local composting facilities.** By doing so, the project follows the principles of the EU's Bioeconomy Strategy and supports forthcoming policy on marine litter and plastic use.

It is important to balance the functionality and biodegradation behaviour of the bio-based ropes when developing the proper bio-based formulation for the aquaculture sector. With its research, prototype development, and pilot tests **BIOGEARS** aims to fill the current technological gaps and to boost the use of bio-based materials in the sector.

As part of the project, **BIOGEARS** works with a concept called Blue Lab, which is an innovative laboratory to pilot new and economically viable solutions to address a marine challenge, in this case plastic litter in the marine environment, a hot topic in ocean governance. The consortium teams up research and industry stakeholders, combining multidisciplinary competences, to together develop innovative ropes in support of a thriving and sustainable blue economy in Europe. The Blue Lab concept works at the interface between research and commercial exploitation, testing and piloting innovative products and services so that results from research are taken forward closer to the market. In BIOGEARS the Blue Lab will also support the replication of research and its implementation in other European Regions. BIOGEARS will conduct technical, economic and environmental analysis of the biodegradable ropes' performance, both at lab and pilot scale (sea tests).

As the only project within the EMFF-BlueEconomy-2018 (Blue Labs) call that has a geographical focus on the Atlantic Basin, BIOGEARS therefore represents an exciting research area for this region.

There are five partners in the consortium: AZTI, GAIKER and ITSASKORDA from Spain, Centexbel from Belgium and Intrigo from Ireland.

Project coordinator: AZTI (Spain) - Leire Arantzamendi Egiguren (larantzamendi@azti.es)

Project communication, dissemination and outreach partner: INTRIGO Ltd (Ireland) - Jane Maher (jane@intrigo.eu)

More information coming soon on https://www.biogears.eu

Centexbel: Lien Van der Schueren | lsc@centexbel.be | https://www.centexbel.be/en/projects/biogears

BIOGEARS (2019-2022) is funded by the European Union EASME EMFF programme under the EMFF-0102018 Blue Labs call.

1 Integrated multi-trophic aquaculture (IMTA) is the co-cultivation of fed species (such as finfish or shrimp) together with extractive species, such as suspension-feeding (e.g., mussels and oysters) and deposit-feeding (e.g., sea-cucumbers and sea-urchins) invertebrates and macroalgae (e.g., kelps), which may feed on the organic and inorganic effluents generated by the fed species. By establishing such integrated cultivation systems, the sustainability of aquaculture may be increased (Chopin et al., 2001; Neori et al., 2004; FAO, 2006; Buchholz et al., 2012). However, in order for IMTA to be economically viable, each of the individual components must be marketable (Chopin et al., 2008), or adding value through accounting for the ecosystem services that extractive species provide (Buchholz et al., 2012).

Interreg
2 Seas Mers Zeeën
European Regional Development Fund
EUROPEAN UNION

SeaBioComp

There is an increasing demand for composites for applications in a marine environment due to the growing markets for fish and seaweed farming, energy harvesting, boats, pontoons, anchoring and buoy elements, etc. At present only petrol-based composites are being used. Concern is growing about the long-term ecological impact. Litter and microplastics are contaminating the sea, having a detrimental impact on sea-life. There is a need for renewable materials to be developed; reducing the depletion of the fossil based materials, limiting emission of greenhouse gases and reducing ecotoxic impact of microplastics. At the same time, the materials need to meet the highest technical performance and withstand the long term harsh marine environment including mechanical forces, aggressive environment, intense UV light etc. Meeting this duality is a major challenge. SeaBioComp is aiming to address this challenge.

Contact: Gertjan Vancoillie | gvc@centexbel.be

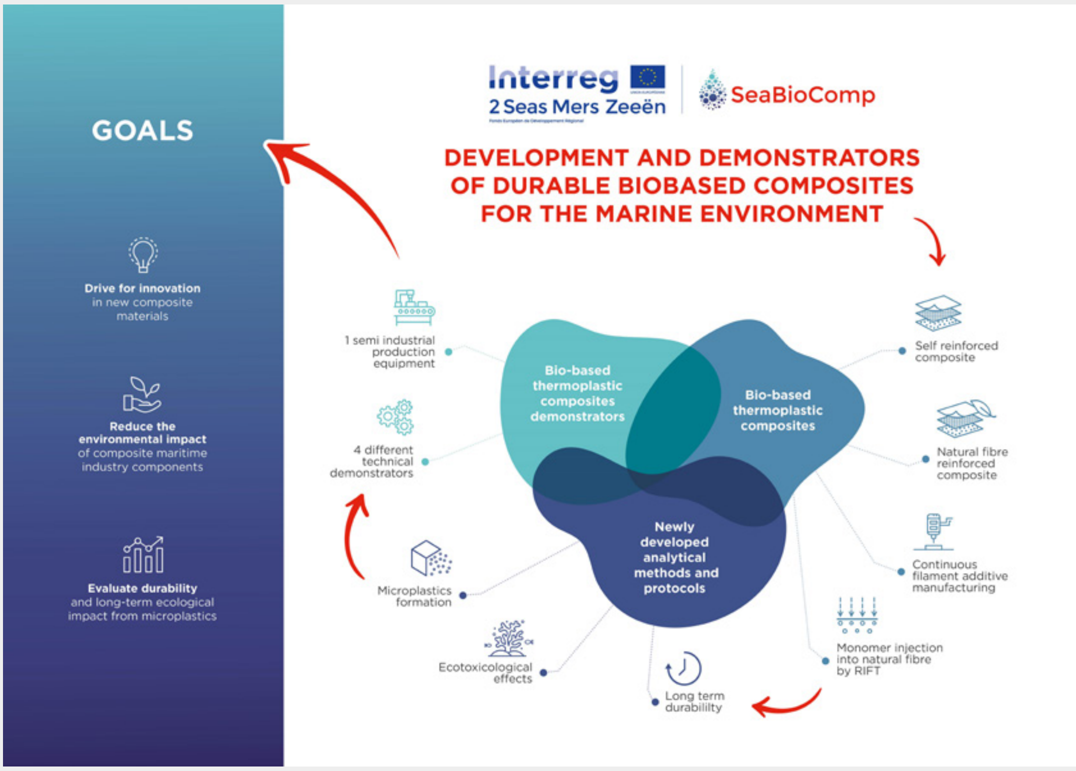
The project will develop 'demonstrator' bio-based composite alternatives to potentially replace traditional fibre-reinforced composites commonly used in the marine industries. Traditional oil-based products including fishing and seaweed farming components, energy harvesting equipment, boats, pontoons, anchoring and buoy parts are potentially being addressed by the project. The bio-composites will not only reduce the depletion of fossil-based resources but should also limit the emission of greenhouse gases and the ecotoxic impact of microplastics, while allowing recycling through the use of thermoplastic bio-polymers. Through the development of the bio-composite demonstrators, the project aims to significantly shift the perception within the marine industries that the use of bio-based composites can offer a realistic and viable alternative. The demonstrators and developed analytical protocols will help both industry and public authorities to address the growing concern regarding the global production and consumption of oil-based plastic materials and the long-term ecological impact of plastic litter and microplastics in the marine environment.

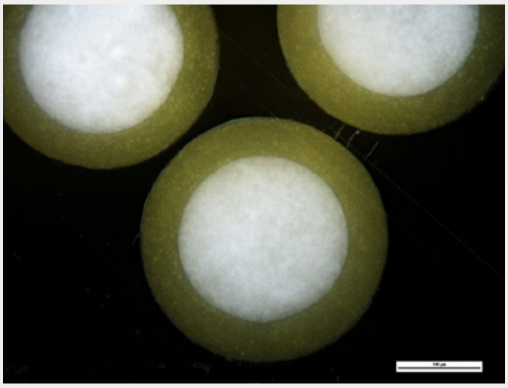
SeaBioComp wants to deliver demonstrators of innovative bio-based thermoplastic composites; with

- at least equivalent mechanical properties
- with -application dependent- tailored durability (2 to >20 years)
- with reduced CO_2 emission (30%), and reduced ecotoxic impact due to microplastics and leachates

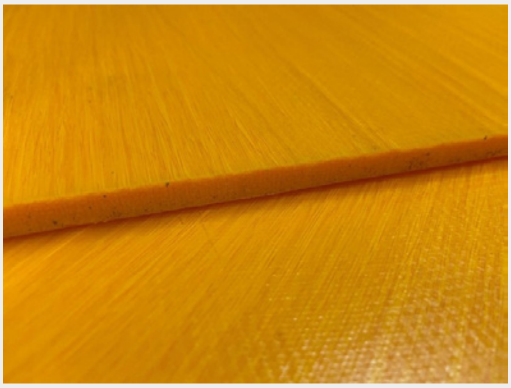
Since thermoplastic composites are envisaged, the recycling potential of recovered materials will be demonstrated as well. Overall the ecologic impact should be reduced by >50% compared to conventional oil-based counterparts. This should lead to a shift in mindset along the value chain, that the bio-based composites offer a realistic alternative for the oil based counterparts.

One possible route that will be explored is the use of bio-based, self-reinforced thermoplastic polymer composite. By using a bicomponent extrusion technique available at Centexbel and CETI, filaments will be developed containing a high melting thermoplastic biopolymer as core with a layer of low melting thermoplastic biopolymer around it as sheet. After winding these bicomponent filaments on a frame, composites will be made using conventional compression moulding at IMT-Lille Douai. By carefully selecting the parameters of the compression moulding process, the sheet will melt and acts as matrix around the solid high melting cores creating unidirectional fibre-reinforced composites. Currently, the mechanical properties of the composites are further optimized and the first marine aging studies are underway. In the next steps of the SeaBioComp project, these bio-based, self-reinforced thermoplastic polymer composite will be further strengthen by combining them with flax-reinforcement fibres.





Microscopic cross-section of core/sheet bicomponent filaments



fabricated unidirectional bio-based composites within SeaBioComp.

The project partners include research institutions, university research groups, SME's and specialist cluster organisations. SeaBioComp is co-funded under the EU Interreg 2 seas programme, within the Technical Innovation theme. SeaBioComp runs from March 2019 to August 2022 with an overall budget of €4.1M, €2.5M of which (60%) is funded from the European Regional Development Fund.

SeaBioComp is led by Centexbel (BE) and combines experts in polymer research, textile and composite formation with marine institutes, sector cluster organisations and public authorities.

Anyone interested in this important and growing area of bio-based materials for the marine environment is invited to join the Interest Group at www.seabiocomp.eu/interest_group/

Subscribers to the Interest Group will be kept informed of relevant events and forums, project activities, results etc. The aim of the Interest Group is to stimulate inclusive engagement of external stakeholders and interested parties including the triple helix of academia, industry and public authorities.

http://www.seabiocomp.eu/

Finding the right methods for measuring microplastics in water

Source: https://ec.europa.eu/jrc/en/news/finding-right-methods-measuring-microplastics-water

The Joint Research Centre (JRC) launched an inter-laboratory comparison study to identify and harmonise methods to measure microplastics in water. There is an emerging concern regarding the impact of microplastics on human health. Further research is needed to make a credible judgement of the risk.

Microplastics are tiny pieces of plastics that are increasingly reported to contaminate the water we drink, the food we eat and the air we breathe.

Where do microplastics come from?

Microplastics can be intentionally produced and added to products for a specific purpose, for example as exfoliating beads in facial or body scrubs. They can be formed during the lifecycle of plastic products, e.g. by abrasion of tyres or fibres released from synthetic cloths. Microplastics can also be formed through degradation of plastic articles released into the environment, e.g. by inappropriate waste management.

What is the EU doing in the field of microplastics?

In 2018, the European Commission proposed new EU-wide rules to target the 10 single-use plastic products most often found on Europe's beaches and seas, as well as lost and abandoned fishing gear. Together these constitute 70% of all marine litter items.

The EU Plastic Strategy contains a comprehensive approach to reducing the emission of microplastics from all sources.

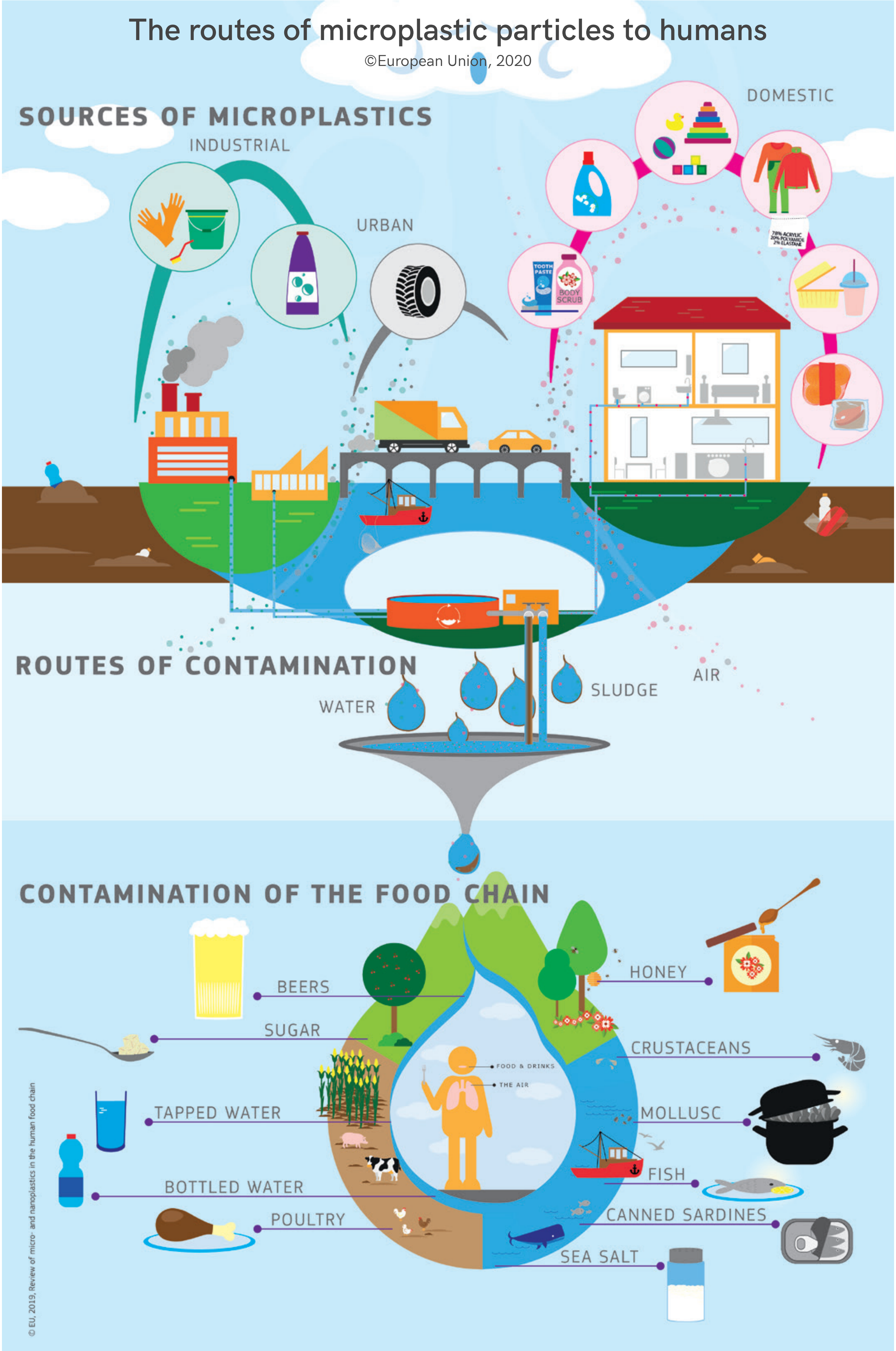
Under the European Green Deal, addressing emissions from microplastics will be one of the Commission's priorities.

The Commission envisages focused actions to limit the emission of microplastics from the use of products such as tyres and textiles, and from primary plastic production.

The Commission is also working on a restriction of microplastics intentionally added to consumer or professional products, such as cosmetics, paints or detergents.

The new Drinking Water Directive empowers the Commission to develop a methodology to measure microplastics with a view to including them on the watch list.

As a follow-up to the Evaluation of the Urban Waste Water Treatment Directive, the Commission will also look at methods to measure microplastics in the influent and effluent of wastewater treatment plants as well as how removing microplastics from wastewater increases the concentration of microplastics in the sludge.


The routes of microplastic particles to humans
©European Union, 2020
SOURCES OF MICROPLASTICS
INDUSTRIAL
URBAN
DOMESTIC
TOOTH PASTE
BODY SCRUB
ROUTES OF CONTAMINATION
WATER
SLUDGE
AIR
CONTAMINATION OF THE FOOD CHAIN
BEERS
SUGAR
TAPPED WATER
BOTTLED WATER
POULTRY
HONEY
CRUSTACEANS
MOLLUSC
FISH
CANNED SARDINES
SEA SALT
FOOD & DRINKS
THE AIR
© EU, 2019, Review of micro- and nanoplastics in the human food chain

Biodegradability in marine environments

Currently, there is no standard providing clear pass/fail criteria for the degradation of plastics in sea water. The US standard ASTM D7081 "Standard Specification for Non-Floating Biodegradable Plastics in the Marine Environment" has been withdrawn in 2014 without replacement.

However, the test methods US standard ASTM D7081 referred to are still in place, but do not offer any pass/fail criteria: ASTM D6691 "Standard Test Method for Determining Aerobic Biodegradation of Plastic Materials in the Marine Environment by a Defined Microbial Consortium or Natural Sea Water Inoculum", ASTM D6692 "Standard Test method for Determining the Biodegradability of Radiolabelled Polymeric Plastic Materials in Seawater" and ASTM D7473 "Standard Test Method for Weight Attrition of Plastic Materials in the Marine Environment by Open System Aquarium Incubations".

Other relevant standards are OECD 306 "Biodegradability in sea water" and ISO 16221 "Water quality – Guidance for determination of biodegradability in the marine environment".

On ISO-level, standardisation efforts for the requirements for biodegradation of plastics in marine environments are well underway. ISO 18830 and ISO 19679, for example, are two standards on the test methods for determining the aerobic biodegradation of non-floating plastic materials in a seawater/sediment interface, both of which have been published in 2016 and are also eligible on CEN-level. ISO 22404 for the determination of aerobic biodegradation of non-floating materials in marine sediments has been published in 2019. The draft standard ISO/CD 22766 for the disintegration test of plastic materials in marine habitats under real field conditions is currently under development. The draft standard ISO/DIS 22403 will include test methods and requirements of the inherent aerobic biodegradability and environmental safety.

However, these standards are only guidelines and do not provide clear requirements for conditions and timeframes.

Research and development is on-going to create harmonised standards for marine biodegradation, which are needed before relevant products can be introduced to the market. With research underway and standards and certified products likely to see the light of day in the near future, questions concerning the limitations for this technology need to be answered: In which context and for which products does this technology make sense and how can it complement a circular economy? Once these questions have been answered, sound communication and advertising rules need to be defined.

Source : www.european-bioplastics.org (September 2019)

Centexbel contact: Karin Eufinger, Standardisation Manager | ke@centexbel.be

TÜV AUSTRIA Belgium (former Vinçotte) has developed a certification scheme based on ASTM D7081, which demands a biodegradation of at least 90% in 6 months. The corresponding label is OK biodegradable MARINE. However, the certification scheme makes a clear distinction between the certification of the claim and the authorisation to communicate about it.

Carbon fibres made from lignin-PLA blends

Lignin, a constituent of wood holds the cellulose fibres and the hemicellulose together. It is a by-product of the paper and pulp industries, and therefore an inexpensive and abundantly available biopolymer, that has already been studied for its value as flame retardant, antioxidant, polymer filler, and as feedstock for the production of carbon fibres.

Sofie Huysman | shu@centexbel.be

In this article, we will address the potential of lignin for the production of porous carbon fibres. Porous carbon fibres are used in non-structural applications, including filtration and electrochemical processes for energy storage platforms in cars and aircrafts.

Because lignin is a bio-based, inexpensive and easily available waste material, it is an ecological alternative to the commonly used fossil-based PAN as a carbon fibre precursor.

However, lignin processing is not self-evident because of extensive cross-linking and strong intra-molecular interactions. These constraints can be overcome and more desirable properties can be obtained by polymer blending.

Within the LIBRE project, we have produced continuous lignin-based fibres by making a careful polymer selection and by closely controlling the processing conditions.

1. Material selection and characterisation

The processing requires lignin with a thermoplastic behaviour. The selected lignin is a modified hardwood type. To evaluate the thermal behaviour, we have carried out DSC and TGA measurements on non-dried samples with a water content of 3%.

A heat-cool-heat run was performed with heating and cooling rates of 10°C per minute. The cooling curve showed no crystallization peaks, which is an indication of the amorphous nature of lignin. The second heating curve reveiled a glass transition temperature (T_g)[1] of 109°C.

We also evaluated the thermal stability by thermogravimetric analysis (TGA). We registered that a weight loss between 1% and 5% corresponded with a temperature rise from 229°C to 277°C. The melt flow index at 200°C is approximately 3.8 g/10 min.

We produced blends by mixing lignin with polylactic acid or PLA, a thermoplastic polymer derived from renewable resources like corn, starch or sugar cane. Therefore, we tested two PLA grades: 6400D (produced by NatureWorks) and L130 (produced by Corbion).

In addition we tested blends composed of lignin, PLA and polyethylene glycol (PEG, M_w 8000). As PEG acts as a plasticizer for lignin, and because both lignin and PLA are rather brittle materials, PEG could improve the processability of the blend.

1 Temperature region where the polymer transitions from a hard, glassy material to a soft, rubbery material

2. Lignin-PLA & Lignin-PLA-PEG blends production

The PLA granulates and lignin powder were first dried in an vacuum oven at 80°C to prevent hydrolysis during the extrusion. To obtain sufficiently high carbon yields, a lignin content of minimum 50% was chosen.

The materials were blended in a semi-industrial twin-screw compounder at 190°C. The extrudates were pelletized after cooling in a water bath. The properties of the blends were characterized by DSC and TGA analysis. The glass transition temperature of all blends remained close to 60°C. The melting point of the PLA L130 blend is a bit higher than for the PLA 6400D blends, see table. Based on the TGA measurements, we were able to obtain a carbon yield (CY) between 20 and 24%.

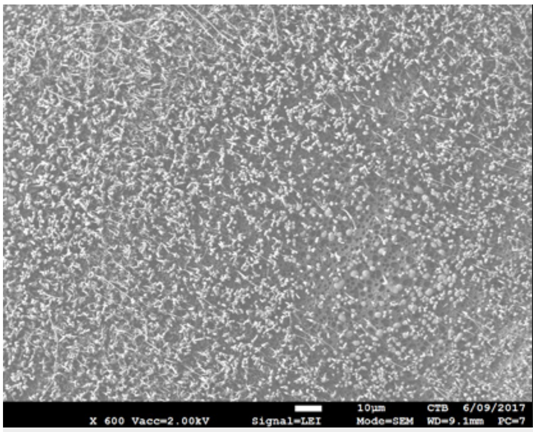
	T_m (°C)	CY (%)
50/50 Lignin/6400D	156-165	23,7
50/45/5 Lignin/6400D/PEG	157-166	20,9
50/45/5 Lignin/L130/PEG	171	22,2

3. Precursor fibre production

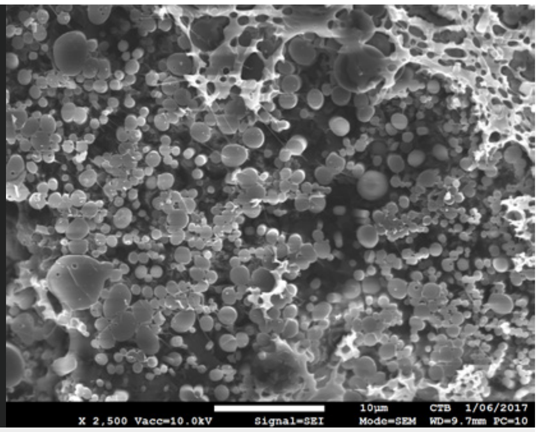
All blends were processed on a semi-industrial monofilament and multifilament extrusion line, using a temperature profile from 175°C to 195°C. The blends without PEG are very brittle and could not be wound without breaking. The addition of 5% PEG improves the processability. The brittleness is strongly reduced and it is possible to wind the filaments.

The picture shows the phase separation: PLA fibrils are formed within a lignin matrix. This indicates the low compatibility between the lignin and the PLA.

Lignin-PLA blend without PEG



cross-sections of the filaments

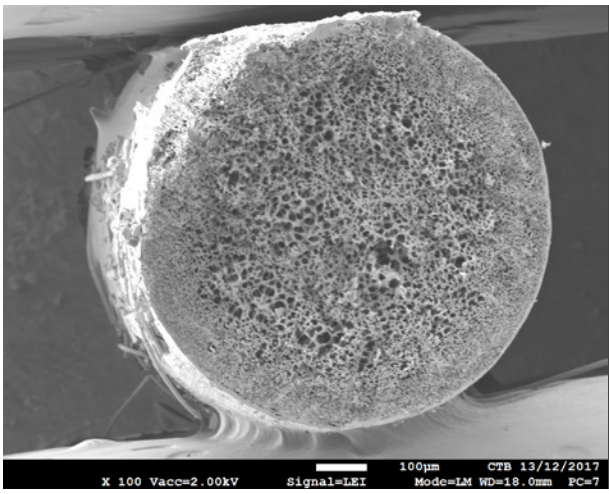


Blends containing 5% PEG produce smaller fibrils (<1 µm), that are more uniform in size and more evenly distributed within the matrix. This correlates with the improved processability. Furthermore, the blends composed of PLA grade L130 is easier to process than the one made from PLA grade 6400D.

4. Porous carbon fibre production

In the final step, we transformed the best performing blend (i.e 50% lignin, 50% PLA L130 and 5% PEG) into carbon fibres. This test was performed at lab-scale. The fibre was first stabilised in O_2 to 250°C, followed by carbonisation in N_2 to 1000°.

With further research and optimisation, these porous carbon fibres can be optimised for nanofiltration or energy storage applications, offering an alternative for complex and less sustainable methods such as electrospinning.



SEM image of the cross-section of the produced carbon fiber showing a porous structure caused by the phase separation between lignin and PLA.

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100% bio-based TPE
Pipedream or maybe not?

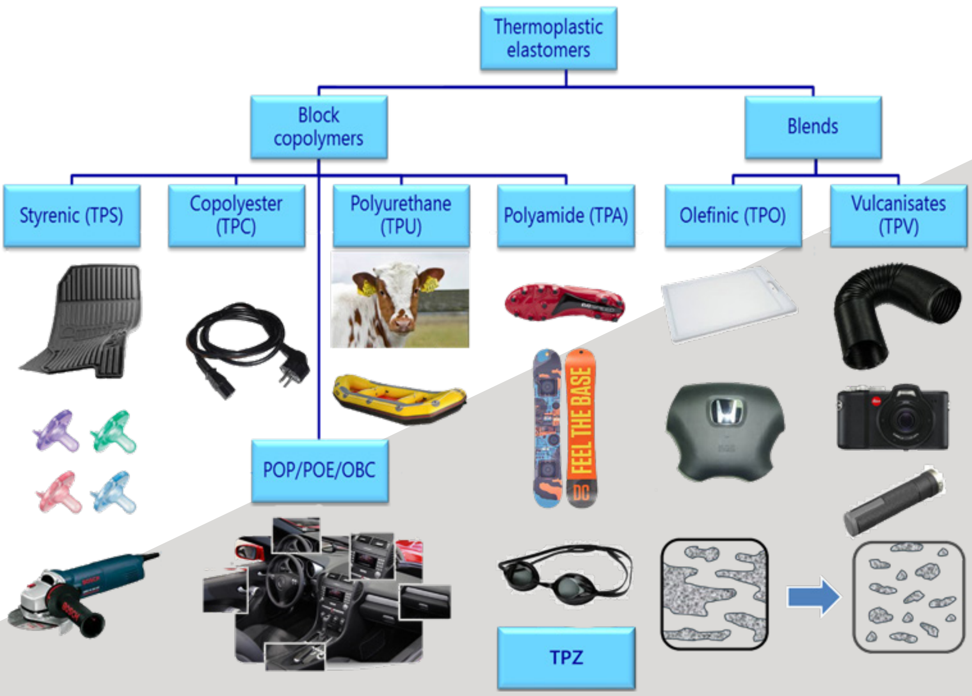
Thermoplastic elastomers (TPE) are plastics that combine the properties of classic elastomers (flexibility, elasticity) with the processability of thermoplastics. Most conventional thermoplastics tend to have low wear resistance and flexibility. TPE can be used as an alternative to meet these desired requirements. In addition, the impact strength of conventional thermoplastics can be improved by adding a TPE.

Stijn Corneillie | sco@vkc.be - Anneke Saey | as@centexbel.be - Isabel De Schrijver | ids@centexbel.be

Thermoplastic elastomers are one of the fastest growing markets within the plastics industry worldwide (annual >6%). The possibilities of TPE are endless. They are widely used in the automotive industry, but are also increasingly being applied in the medical, food and sports articles sectors. The flexible and elastic properties as well as the soft feel of TPE are key factors here.

TPE can be divided into different classes. A first classification is based on the TPE's structure. Most of the commercially available TPE are block copolymers, consisting of 2 or more polymer chains linked together: styrene-based TPE (TPS), copolyester TPE (TPC), copolyamide TPE (TPA), polyurethane-based TPE (TPU) and recently also olefinic block copolymers (POP, POE, OBC) have been added.

The second "class" of TPE consists of a mixture (or blend) of different polymers: olefinic TPE (TPO) and dynamically vulcanised TPE (TPV). TPE which do not belong to these classes are included in a separate class and may therefore be either block copolymers or blends (TPZ). The different classes, as well as some typical applications, are illustrated below.



TPE, like most plastics, are synthesized from petroleum-based raw materials. Because ecological awareness is growing among customers, they insist on sustainability and bio-based as being desired product properties. This prompted the industry to invest more in research into bio-based, 'green' alternatives to conventional plastics. As TPE are a recently developed class of plastics, research on bio-based TPE is still in full development.

In 2010 the company Braskem succeeded in producing polyethylene (PE) on an industrial scale from sugar cane[1]. Polyolefins are often blended with TPS to confer a certain hardness and mechanical strength to the material. The use of bio-PE from sugar cane (as an alternative to petroleum-based PE) led to the first bio-based TPE, which is generating increasing interest.

This was the kick-off for further research into bio-based TPE. In the years that followed, more and more possibilities were explored by the industry. This not only resulted in more bio-TPE, but also in bio-TPE with new and improved properties. The company Kuraray won ß-farneseen from sugar cane, which can serve as a building block for bio-TPS with damping properties[2]; the company Covestro researched numerous bio-based polyols from sugars for bio-TPU and the company Arkema developed bio-TPA from PA11, which was produced from bio-based oil extracted from the Castor Plant[3].

Despite these many developments, not a single TPE that is 100% bio-based is currently being produced on an industrial scale. These developments always contain a percentage of non-bio-based raw materials. The main reasons why 100% bio-based TPE are not industrially available are, on the one hand, the cost price (which increases significantly with the use of a higher percentage of bio-based raw materials) and, on the other hand, the decrease in mechanical properties. Research on bio-TPE is on-going.

In het Interreg-project ‘Elasto-Plast’[4], we are looking together with our partners to solve the problem of 100% bio-TPE at an acceptable price. The research group of Prof. Dr. Ir. Wim Thielemans (Chemical Engineering Group, KULeuven department Kortrijk) analyses the possibility of synthesizing 100% bio-TPE from sugars. The properties and industrial applicability are then evaluated by Centexbel. The project runs until March 2021.

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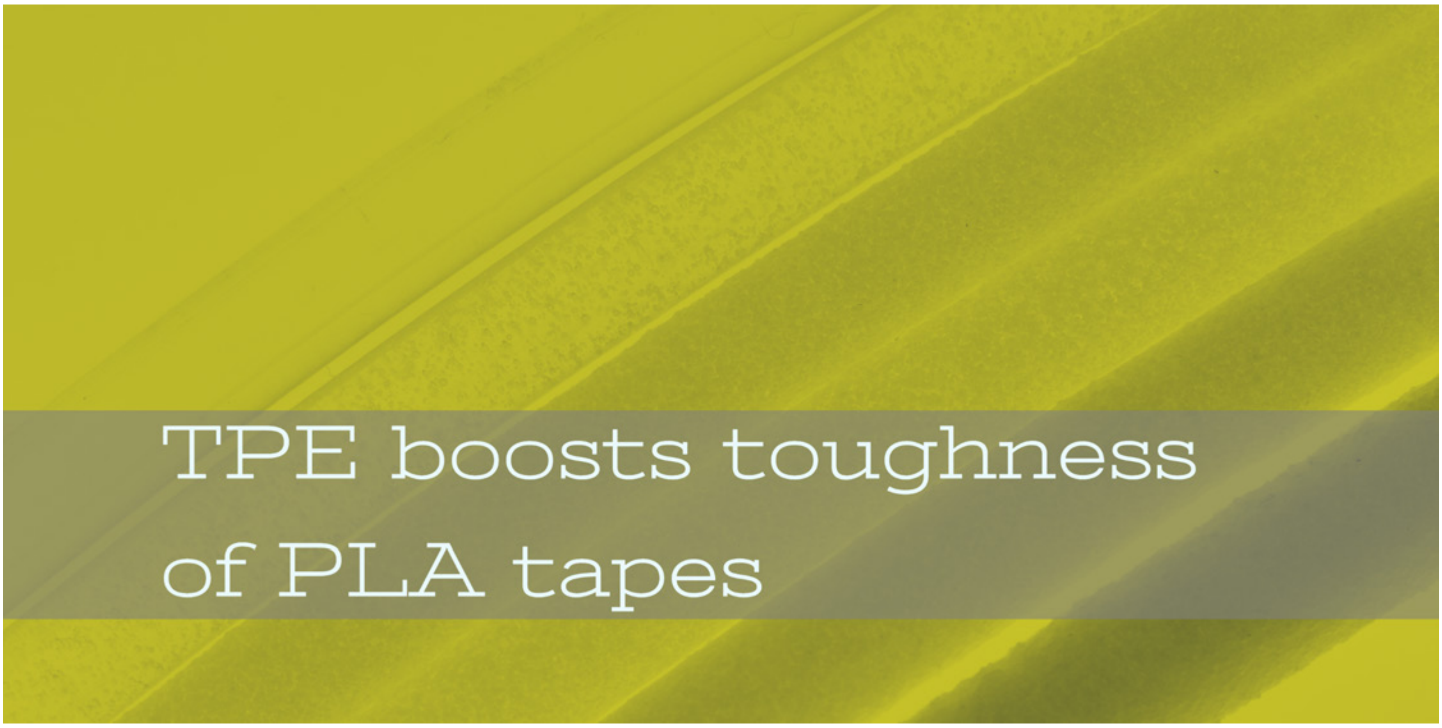
FINANCEMENT FEDER - EFRO-FINANCIERING : 1.303.181,15 € | COÛT TOTAL - TOTALE KOST : 2.369.420,32 €

1 http://plasticoverde.braskem.com.br/site.aspx/Im-greenTM-Polyethylene
2 Kuraray, Development of a new styrenic elastomer using renewable monomer, TPE Magazine, 2015, 262-263
3 Sebasien Merzlic, Towards a new generation of Pebax elastomers, TPE World Summit Milan, 2018
4 https://interreg-elastoplast.eu



TPE boosts toughness of PLA tapes

PLA (polylactic acid) is produced from biomass and has special piezoelectric properties, i.e. it can convert mechanical strain into electrical charges. At present, these properties are hardly exploited. The **BIOHARV**-project[1] optimises the formulation and production processes of PLA-based mono-oriented films, tapes and fibres to enable the use of these materials in new micro-energy recovery applications for the power supply of smart and communicating sensors.

Stijn Corneillie | sco@vkc.be - Birgit Stubbe | bst@centexbel.be

PLA has many advantages, in addition to its renewability, it has high mechanical strength and is relatively easy to process. However, its inherent brittleness is an important drawback that significantly limits a wide application of the material. This brittleness also proved problematic in the production and processing of PLA tapes for energy recovery prototypes. The tapes were very difficult to handle due to splitting along the machine (i.e. longitudinal) direction . A common strategy to improve the properties of (bio-based) plastics is to mix them with plasticisers or more flexible polymers. This is also an efficient, cost-effective way to increase the toughness of PLA. The use of flexible polymers is particularly interesting because of the limited loss in tensile strength and modulus of elasticity compared to the application of plasticisers, provided that a fine morphology and suitable compatibility of mixtures can be obtained[2].

An interesting type of materials in this context are thermoplastic elastomers (TPE), a collective term for plastics that are elastic at room temperature and become plastic and can be reshaped when heated. These plastics combine the properties of classic elastomers (flexibility, elasticity) with the processability of thermoplastics. Most conventional thermoplastics exhibit rather low wear resistance and flexibility. TPE can be used as an alternative to meet these desired requirements. In addition, the impact strength of conventional thermoplastics can be improved by adding a TPE. The **ELASTOPLAST**-project[3] aims at gathering knowledge about the relationship between morphology, process conditions and product properties of TPE as well as the new developments in of the field of this unique technology. The main goal of the project is to familiarise companies with the rich possibilities that TPE offer to increase product properties or improve the processability of classical polymers.

1 http://www.gotos3.eu/bioharv
2 Ming Wang, Ying Wu, Yi-Dong Li & Jian-Bing Zeng (2017): Progress in Toughening Poly(Lactic Acid) with Renewable Polymers, Polymer Reviews, DOI: 10.1080/15583724.2017.1287726
3 https://interreg-elastoplast.eu/

The acquired knowledge from both above mentioned projects was used to develop PLA tapes with improved mechanical properties. For this purpose, a SEBS-based TPE (Thermolast®K TF7ADN from the Kraiburg company) was selected, as it previously gave good results in PLA injection moulding applications. This TPE was compounded with PLA (Luminy® L130 from the Total Corbion company) in different proportions (from 1 to 10%) and then processed via tape extrusion. The effect of the TPE became apparent at macroscopic level starting from a concentration of 5%. The tapes (thickness 40-70 µm, width 11-14 mm) evolved from transparent, slightly undulated tapes that split very easily along the machine direction to matte-white, smoother tapes that no longer show any cracks, even at higher draw ratio (DR), as shown in Figure 1.

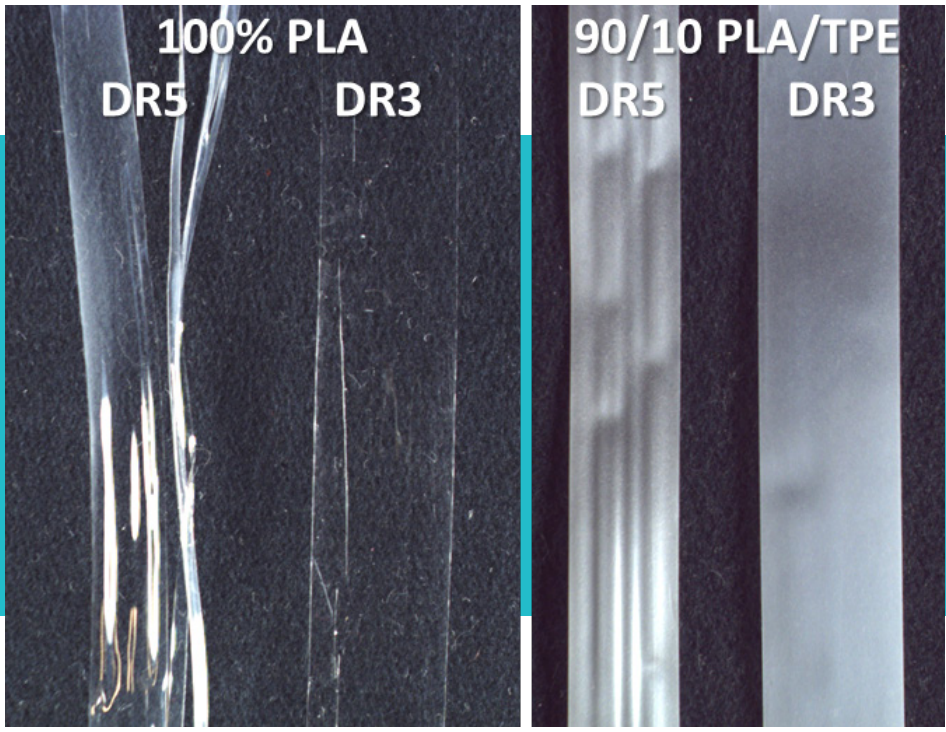


Figure 1 Pure PLA tapes (left) versus 90/10 PLA/TPE-blend tapes (right) with draw ratio (DR) 3 and 5.

The mechanical properties of the materials were determined by means of tensile tests in the machine direction of the tapes. The resulting tensile strength (tenacity) and modulus of elasticity (E-mod) of PLA tapes with TPE content ranging from 0 to 10% are shown in Figure 2. The tensile strength appears to show a slight upward trend with increasing TPE content, although the differences are very small, while the modulus of elasticity appears to be unaffected. The TPE therefore has little or no effect on the mechanical properties in the machine direction of the tape.

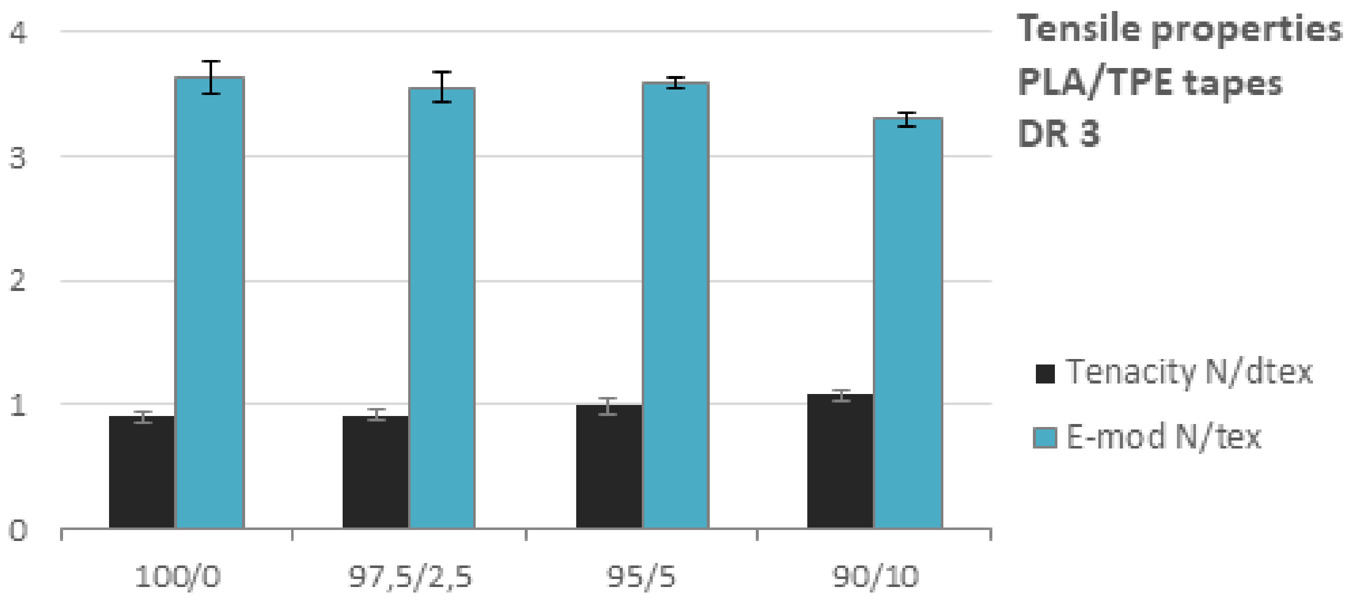


Figure 2 Tensile strength (Tenacity, N/dtex) and modulus of elasticity (E-mod, N/tex) of different PLA/TPE-blend tapes (DR 3).

Due to the limited width of the tapes, it is impossible to determine the strength in the cross (i.e. transverse) direction using the universal testing machines applied for standard tensile tests on yarns (EN ISO 2062) or plastics (ISO 527). It was therefore decided to perform tensile tests in the cross direction of the tapes using DMA ("dynamic mechanical analysis"), a technique that enables the characterisation of smaller samples. The results are presented in Figure 3. The stress-strain plot of 100% PLA clearly shows the course of a brittle fracture, while the 90/10 PLA/TPE tape shows a tough fracture with plastic deformation. The maximum force the materials can undergo is similar, but the maximum elongation of the 90/10 PLA/TPE tape is ten times higher than the elongation of the pure PLA tape. It can therefore be concluded that the TPE has a positive effect on the mechanical properties in the cross direction of the tape.

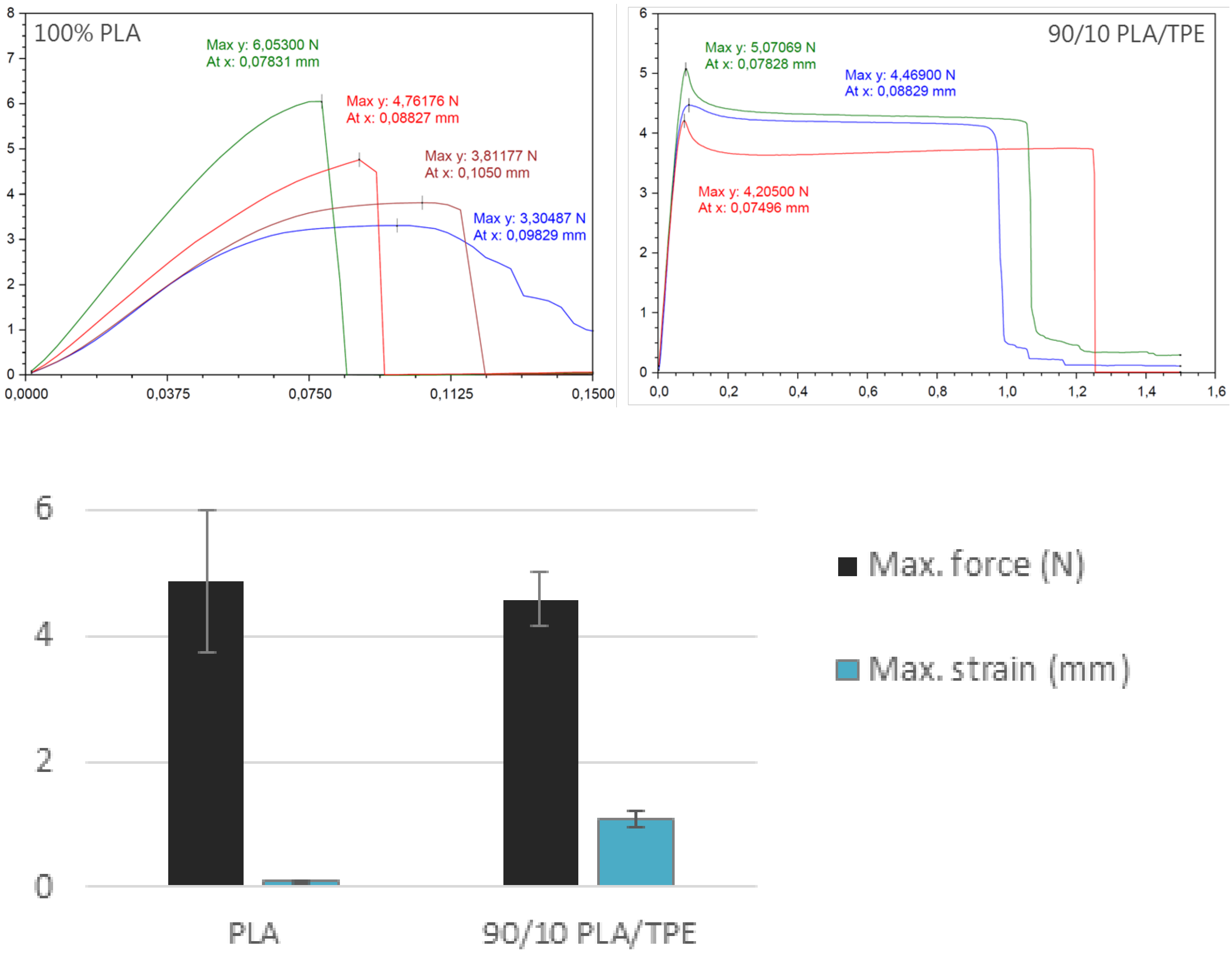


Figure 3 Results of DMA measurements: stress-strain plots (top) and maximum force and deformation (bottom) for 100% PLA and 90/10 PLA/TPE tapes (DR 3).

In order to study the mixing of the TPE and PLA phases, SEM ("scanning electron microscopy") images were taken of the fracture surface of injection moulded test samples. On the electron microscopy images (see Figure 4), two phases can clearly be distinguished: (i) TPE particles dispersed in the (ii) PLA matrix. These rubbery particles can absorb and dissipate part of the distortion energy by means of plastic deformation. The final effect on material strength depends on particle size and dispersion as well as compatibility with the plastic matrix.[2]

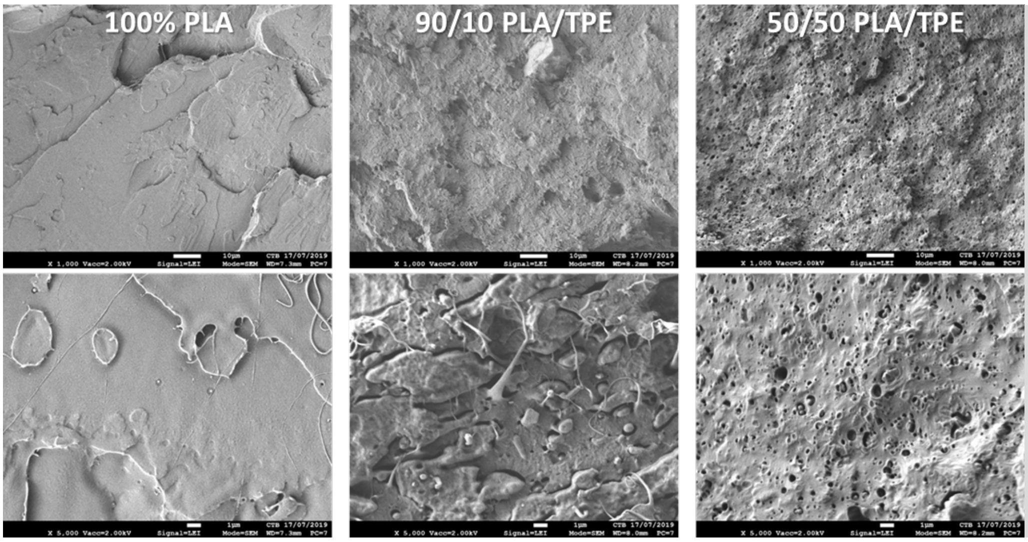


Figure 4
Scanning electron microscopy images of the fracture surface of 100% PLA, 90/10 PLA/TPE and 50/50 PLA/TPE injection moulded test samples.

Finally, piezoelectric energy recovery was evaluated by means of bending tests. Previous experiments with PLA films have already shown that both the crystallinity and orientation of PLA are important factors for higher energy recovery. A higher DR generally leads to a higher polymer chain orientation and crystallinity[3].

The latter was also observed for both pure PLA and PLA/TPE blend tapes, where an increase in DR from 3 to 5 resulted in a twofold increase in crystallinity (from ±20% to ±40%). As the energy recovery measurements had not yet been completed at the time of publication, the data will be published in a follow-up article. However, the first results do not indicate a negative effect of the TPE on the energy recovery capacity of the tapes; on the contrary, the capacity generated by blend tapes generally appears to be higher than for pure PLA. Nevertheless, the effect of the TPE on energy recovery as well as the reproducibility of energy measurements needs to be further investigated before unambiguous conclusions can be drawn.

In general it can be concluded that the addition of 5 to 10% of the SEBS-based TPE TF7ADN leads to an improvement of the mechanical properties of PLA tapes, mainly in the cross direction. The blend tapes also don't show cracking at higher DR and are easier to handle for the production of energy recovery prototypes. Evaluation of the energy recovery is still ongoing, but the first results indicate a positive influence of the TPE on the generated power. Nevertheless, the effect of the TPE on energy recuperation as well as the reproducibility of energy measurements should be further investigated. In addition, different possibilities for further optimization of the crystallinity and the energy recovery capacity will be studied by means of extrusion trials on **Centexbel's monofilament extrusion line**[4].

The extrusion line has four sets of rolls and three ovens (two hot air- and one steam oven) which allows a 3-stage drawing process (instead of a 1-stage drawing). Moreover, the line offers the choice between different cooling methods (water bath, chill roll or air cooling). Finally, it is also the intention to investigate alternative, bio-based TPE as well as the combination with MA-g-SEBS, which could possibly bring about a further improvement in mechanical properties through a better interaction between the two phases.

3 Stubbe, B. et al, Bio-based piëzo-elektrsiche PLA-films voor opkomende IoT-toepassingen, Unitex nr. 1/2019, p.13-16, 1/03/2019
4 https://www.centexbel.be/en/pilot-platforms/extrusion-platform

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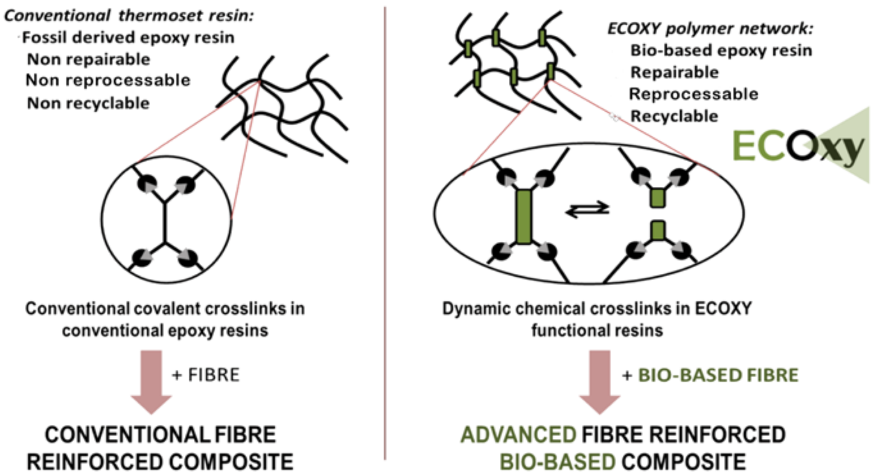
ECOxy "3R" FIBRE-REINFORCED EPOXY COMPOSITES

The Ecoxy project focuses on the development of innovative bio-based composite structures made from a bio-based epoxy resin and a natural or bio-based fibre-reinforcement. Composite products made from these easily renewable natural materials have a strong potential to procure novel biodegradable and/or readily recyclable materials and to replace certain fuel-based polymers/plastics that are currently used in the automotive and construction industries.

Monika Rymarczyk | mr@centexbel.be

The Ecoxy project targets three advanced functionalities: reparability, reprocessability and recyclability (3R). The 3R functionalities will be achieved by using new resin formulations and by replacing commonly used curing agents by dynamic hardeners.



In the field of textile processing, thermoplastic polymeric materials, especially polylactic acid (PLA), are developed to be used as reinforcement. The materials are required to offer a high level of stiffness. Bio-based structures are considered a key trend to arrive at a renewable solution for high performance, and yet recyclable materials with a low carbon footprint.

Several PLA grades were selected and submitted to a yarn spinning process in view of obtaining the defined specifications. To improve the PLA properties, we have tested different techniques, modifications, reinforcements, etc.

The influence of nano-fibrils formation and nano-reinforcement was evaluated by adding higher melting polymers such as polyesters and polyamides. The tests were performed with and without compatibilizers.

It was observed that the properties of the PLA yarns significantly depend on the extrusion processing conditions. During the project we have evaluated standard filament extrusion techniques as well as a two-step procedure which is used to produce high tenacity yarns. We succeeded in obtaining PLA filaments with a tenacity of 4.6 – 5.0 cN/dtex, a modulus of 9.94-9.4 GPa, an elongation of 25% and a shrinkage of 3.81%-4.29%. These yarns were subsequently transformed into woven structures, that are now under evaluation in composite structures.

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This article reflects only the author's view and that the JU is not responsible for any opinion.

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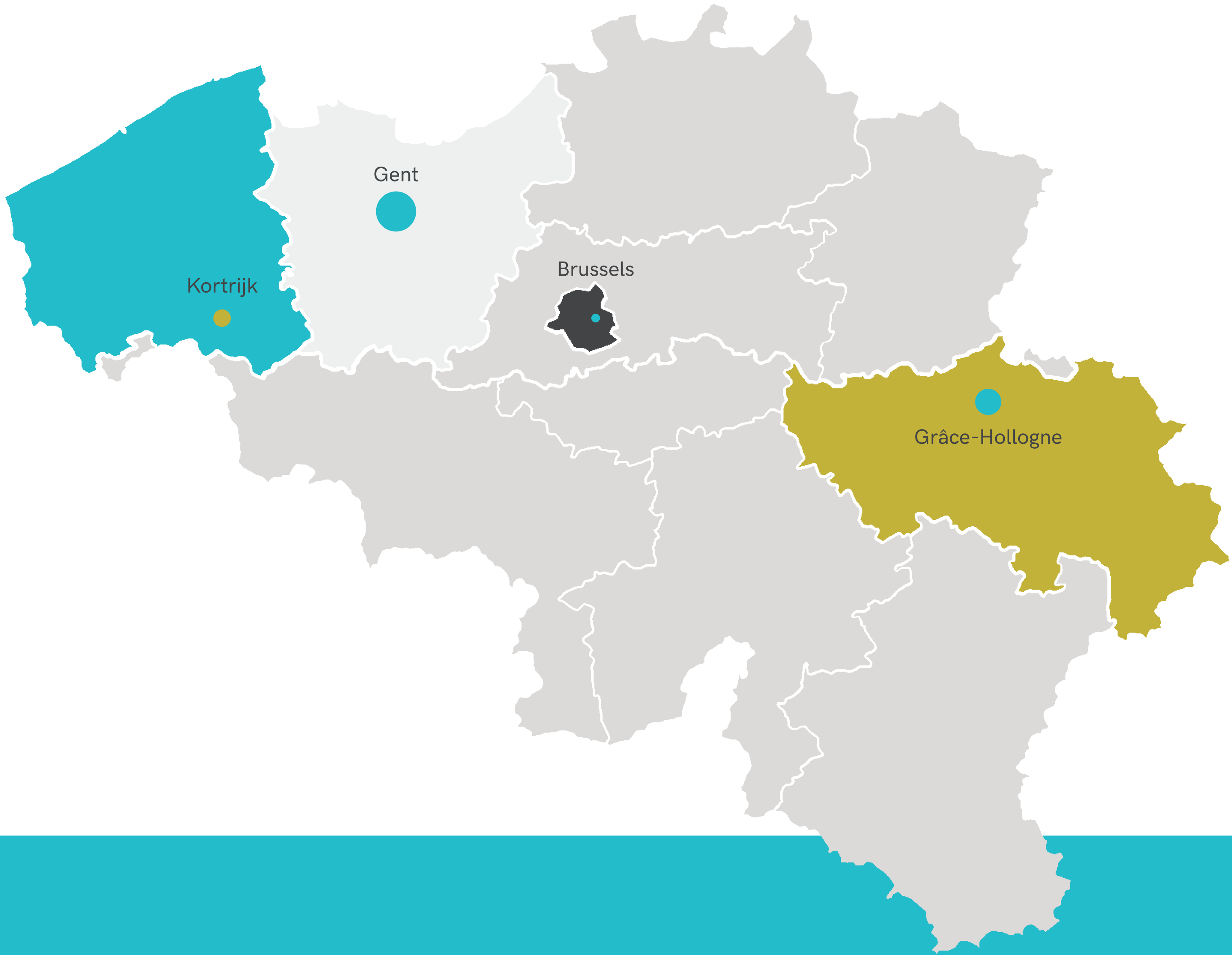

Centexbel-VKC

GENT | Technologiepark 70 | BE-9052 Gent | +32 9 220 41 51 | gent@centexbel.be
KORTRIJK | E. Sabbelaan 49 | BE-8500 Kortrijk | +32 56 29 27 00 | kortrijk@centexbel.be
GRÂCE-HOLLOGNE | Rue du Travail 5 | BE-4460 Grâce-Hollogne | +32 4 296 82 00 | g-h@centexbel.be
www.centexbel.be