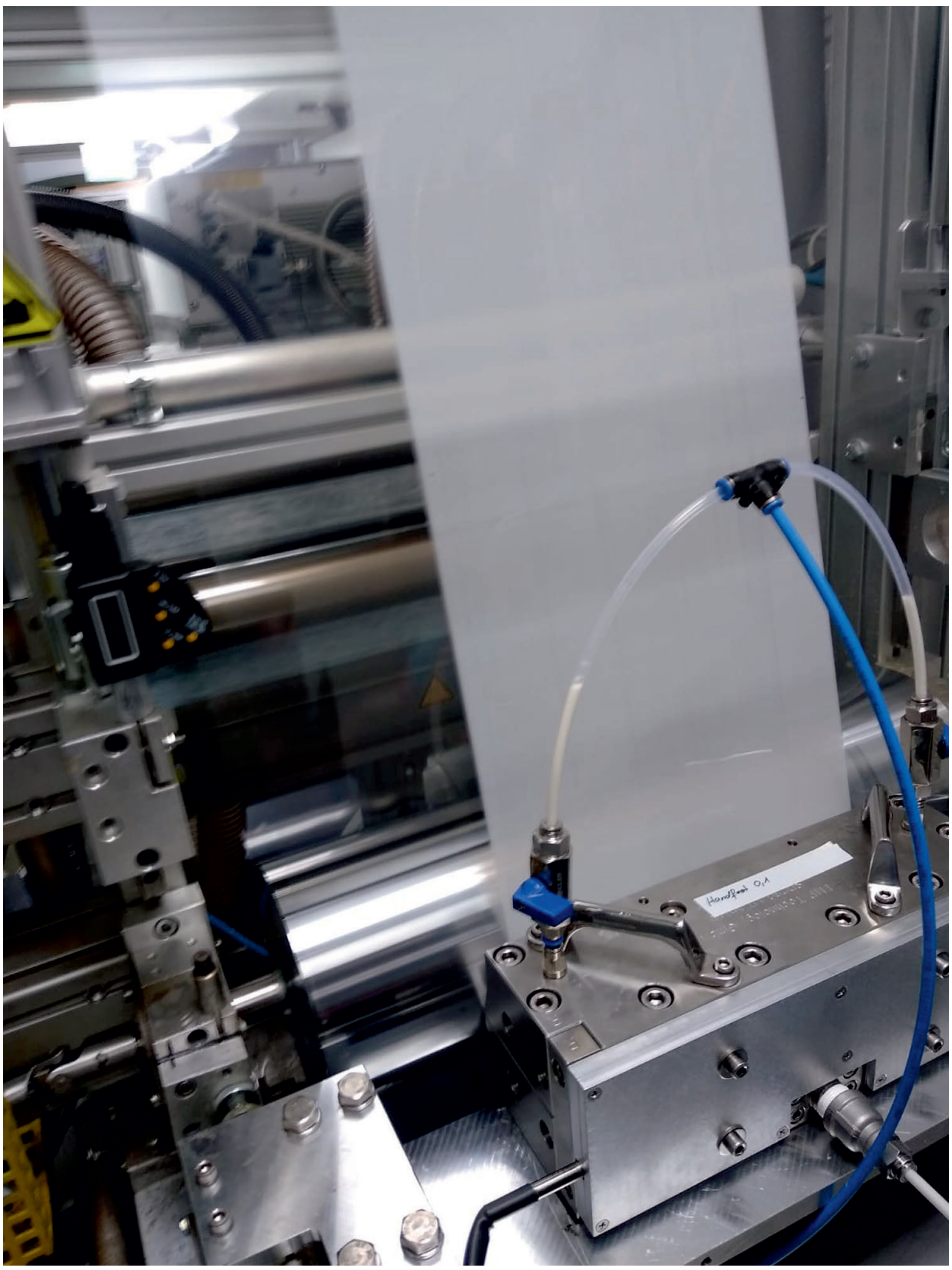
Flexible and Sustainable Plastic Packaging Film thanks to Nanotechnology

Nanoplatelets in a Barrier Lacquer

Within the "BarriFlex" joint project, novel nano-tailored materials with improved barrier properties against gas and water vapor were developed for packaging applications. These materials form the basis of new packaging concepts. Despite intensive research, much still remains to be done as regards diversity of materials, barrier specifications and more efficient manufacturing processes for new, inexpensive, easy-to-recycle and even renewable packaging products.



Production of a demonstrator for a mono-material packaging film. © Fraunhofer IVV

Materials with high barrier properties against oxygen or water vapor are required in many packaging applications, from food to electronics. Since such barrier properties are lacking in commodity polymers, barrier packaging is modified with additional barrier materials. These are usually more expensive than commodity polymers and, in higher fractions, also make recycling more difficult. Current development work is therefore aimed at producing barrier layers that are as thin as possible, but retain the same barrier properties. This paper gives an overview of the results obtained within the Cornet-funded "BarriFlex" joint research project [1].

The aim of the BarriFlex project was to enhance the barrier performance of flexible and transparent plastic films with suitable nanocomposite coatings that are compatible with large-scale roll-to-roll production lines. Two different broadly based but complementary applications were targeted:

- food packaging and
- photovoltaic (PV) encapsulation.

Along with the barrier properties, the relevant products will also offer benefits such as recyclability, as well as lower production and material costs.

Nanolacquer Formulation

While the results of the project will feed directly into the food packaging industry, the technology for photovoltaics encapsulation is still somewhat exploratory. Organic and hybrid PV (OHPV) have recently emerged as a promising low cost, versatile and flexible technology

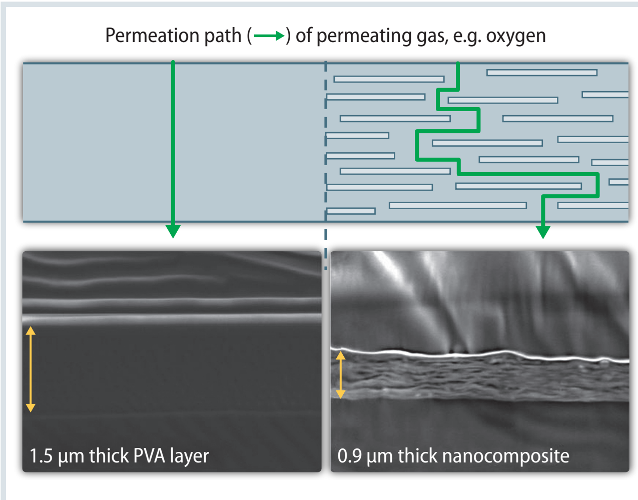


Fig. 1. Top: the integration of platelet-shaped, impermeable nanoparticles extends the diffusion path. Bottom: scanning electron image of an adequate PVA coating without (left) and with (right) nanoparticles. Source: Fraunhofer IVV; graphic: © Hanser

whose market development is currently limited by inadequate encapsulating solutions, which limit the panels' lifetimes. For both these applications, the project has the effect of reducing the cost, reducing inorganic layers and minimizing the carbon footprint of food packaging, and, in the case of PV, it explores the ultimate trade-off between the simplicity of the device architecture and minimum permeation levels. The project was supported by many small and medium-sized enterprises (SMEs) and companies along the entire value chain, from nanomaterials manufacture, through lacquer and adhesive formulation, surface treatment for robust lamination, and characterization, to food-packaging and photovoltaics manufacturers.

Technically, the project's innovation lies in the concept of a single, yet complex barrier layer achieved by introduction of nanoplatelets into a barrier lacquer, which acts as the polymer matrix. A high-shear mixing process was developed to ensure homogeneous and oriented dispersion of the nanoplatelets. This barrier layer was then coated onto a stretched polypropylene-based (PP) film, and laminated with a polypropylene-based sealing film for food-packaging applications.

Due to the fixing and orientation of the functionalized nanoparticles within the matrix, it is ensured that no migration issues arise. For the encapsulation of flexible PV, the new nanocoating barrier serves as a preliminary encapsulation layer to limit the numbers of complementary layers needed to reach the required permeation levels. In both applications, state-of-the-art barrier performance was achieved in order to demonstrate the added value of the concept.

Manufacture of Mono-Material Laminates for Food Packaging

Many materials used for food packaging need to provide a certain barrier effect against oxygen, e.g. to avoid rancidity, and water vapor, e.g. to retain crispness. In addition to their purely technical performance, they also need to be recyclable. According to most definitions, a recyclable material has to consist of at least 95 wt. % of one material class (mono-material), e.g. polypropylene [2]. The remaining material may e.g. be an adhesive and a barrier layer. A barrier lacquer with platelet shaped nanoparticles was developed in order to elongate the diffusion path for the permeating gas molecules and to create a so-called tortuosity effect as shown in **Figure 1**.

Polyvinyl alcohol (PVA), which formed the polymer matrix, was dissolved in aqueous nanoparticle dispersions, which were prepared by mechanical shearing, to produce the so-called "nanolacquer". These flexible barriers offer technological strengths for rapidly meeting the substantial changes expected in both markets. Nanolacquers with a nanoparticle concentration of 50 wt. % with respect to PVA were coated on a polypropylene substrate film in a single coating step with a slot-die coating unit (**Fig. 2**) in a roll-to-roll pilot line. The integration of 50 wt. % platelet-shaped montmorillonite enhances the barrier perform- »

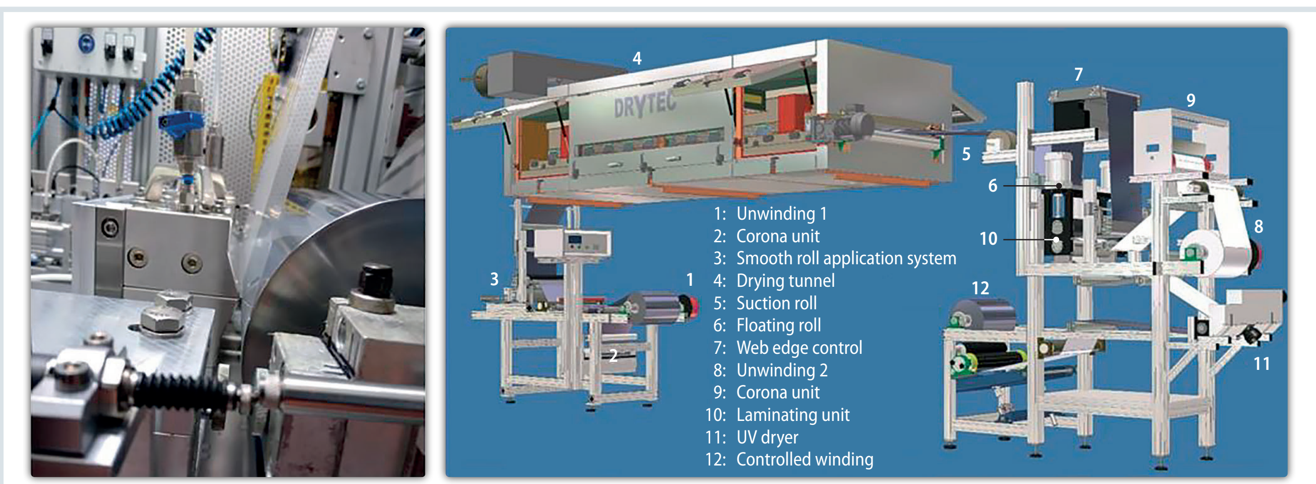


Fig. 2. Left: coating of a PP film with nanolacquer containing 50 wt. % nanoparticles using the slot die technique. Right: schematic diagram of a roll-to-roll coating unit. © Fraunhofer IVV

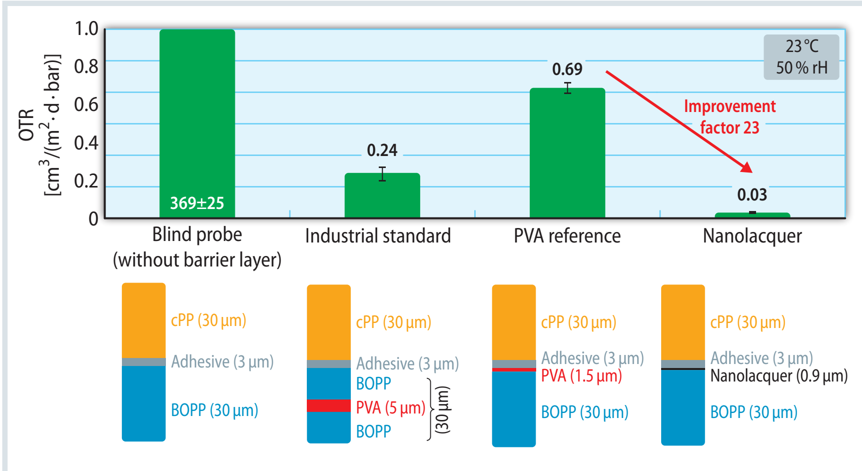


Fig. 3. Oxygen permeation rate for different mono-material laminates. The left bar shows a blank sample without an active barrier layer (to show the differences between the other samples, this bar has been truncated). The industrial standard is a co-extruded high barrier film, which is commercially available. The two samples on the right show the new development within the BarriFlex project and the improvement factor achieved by integrating nanoparticles.

Source: Fraunhofer IVV; graphic: © Hanser

ance by a factor of 23 for oxygen in comparison to pure PVA. Scanning electron microscopy (SEM) shows the parallel orientation of the nanoparticles within the coated layer indicating the tortuosity.

In a polypropylene-based laminated structure, this lacquer provides the barrier against oxygen and the substrate the barrier against water vapor. The oxygen barrier performance of the novel laminates in comparison to conventional-flexible packaging materials is presented in **Figure 3**. These novel recyclable flexible packaging materials were used for production of the food packages as demonstrators within the project.

Atomic Layer Deposition and Laminate Structures for Organic Photovoltaics

In the BarriFlex project, the other application concerns third generation PV cells: organic photovoltaics (OPVs). OPVs offer attractive properties such as lightness, flexibility and semi-transparency. They also stand out for their high absorption making it possible to reduce the thickness of the layers and to promote their integration into applications in which silicon is less efficient, for instance for indoor applications under low light, for portable applications, and addressing aesthetic and design-integration issues in buildings.

However, one of the critical parameters hindering the large-scale marketing of OPVs remains their lifespan. The stability of an OPV cell depends on many factors, for example the materials constituting the light absorbing and converting layer, which are extremely sensitive to water and oxygen and can thus rapidly impair the cell's performance and limit its use over time. High-performance, flexible, transparent, and affordable encapsulation solutions remain a challenge for long term stability along with profitability for industrial developments. In practice, the barrier films must limit the levels of permeation to water vapor and oxygen to extremely low values of the order of 10^{-3} to 10^{-6} g/(m²·day) and 10^{-3} to 10^{-5} cm³/(m²·day), respectively [4].

Atomic layer deposition (ALD) enables low temperature (< 75 °C) conformal deposition of dense thin films (i.e. pin-hole free) with absolute thickness control (atomic scale precision) and uniformity over large areas (> Ø 12 cm). The self-limiting aspect of ALD leads to excellent step coverage and conformal deposition. For barrier applications, ALD provides efficient barrier layers to water vapor ingress that exhibit remarkably few defects, and thus very low permeability.

ALD was used under primary vacuum (< 0.13 bar) for the deposition of dense Al_2O_3 barrier layers on PET/SiO_x substrates typically used in flexible food packaging. The deposition chamber was modified to allow the deposition of Al_2O_3

Info

Authors

Stefan Schiessl is a scientist at the Fraunhofer Institute for Process Engineering and Packaging (IVV), Freising, Germany;
stefan.schiessl@ivv.fraunhofer.de
Esra Kucukpinar is a scientist at the Fraunhofer IVV;
esra.kucukpinar@ivv.fraunhofer.de
Marius Jesdinszki is deputy test manager at the Fraunhofer IVV.
Sandro Gennen is R&D project manager at Celabor, Chaineux, Belgium.
Pascal Viville is project manager and scientific coordinator at Materia Nova R&D Center, Mons, Belgium.
Oliver Douhéret is a scientist at the Materia Nova R&D Center.

References & Digital Version

You can find the list of references and a PDF file of the article at
www.kunststoffe-international.com/archive

German Version

Read the German version of the article in our magazine ***Kunststoffe*** or at
www.kunststoffe.de

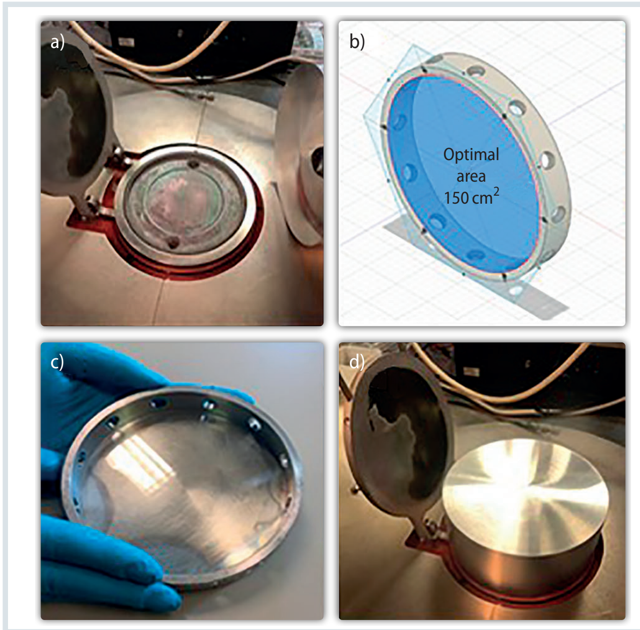


Fig. 4. Optimization of the ALD chamber: (a) initial chamber, (b) schematic and (c) resulting substrate holder specifically made in the BarriFlex project along with (d) modified chamber cap.

on these substrates with an efficient area of 150 cm^2 (**Fig. 4**). We also aimed to limit the number of layers present in the encapsulation film in order to optimize the costs and recyclability, for equivalent performance, by means of a mono-material solution.

Practically, half-systems consisting of PET/SiO_x/Al_2O_3 (Al_2O_3 layer thickness of 20 nm) were produced. In the final architecture of the barrier film, this PET/SiO_x/Al_2O_3 barrier film was laminated with itself in a so-called "face-to-face" structure using a light-curing adhesive. The laminated barrier film thus has the final structure: PET/SiO_x/Al_2O_3/adhesive/Al_2O_3/SiO_x/PET.

This structure is very simple in comparison to the expensive encapsulation solutions commercially available. The water-vapor transmission rate (WVTR) values obtained for the half system and the laminate were 10^{-3} g/(m^2·day) and 10^{-4} g/(m^2·day) respectively. It thus fulfills the objectives and offers an alternative, affordable encapsulating solution.

Conclusions

The developed nanotechnologies enable the production of high-performance, cost-efficient barrier films with low carbon footprint, to cope with current needs in food packaging and encapsulation of flexible photovoltaic systems. In food packaging, the driving forces are the industry's ecological awareness, the "down-gauging" of packaging pledged to consumers and supported by producers, fillers and retailers, and targeting simpler, cheaper yet efficient products. This momentum is driven by European and national directives, which impose severe requirements on recyclability. The development of flexible PV cells is spurred on by the increasing demand for renewable energies, environmental concerns and growing demand for electricity. Flexible PV cells are a strong motivation in many industrial sectors, including traditional PV but particularly emerging OHPV.

Hence, the development of new mono material-based barrier laminates is intended to address these issues and to meet the specific challenges faced by the industry. These flexible barriers offer technical and economic advantages, allowing them to adapt immediately to the substantial changes expected in both markets. ■

PP Copolymer for Cat Food Packaging

Sustainable Retort Pouches

Mars Petcare will use **Sabic**'s BCT18F impact-resistant polypropylene copolymer for the retort pouches of its Sheba cat food brand. The copolymer comes from the company's Trucircle product range and is partly made from recycled PP. The pouches are used to package wet food. The multi-layer film used for this is manufactured by the company Huhtamaki.

"Over the past year, we have been closely working with Sabic and Huhtamaki, continually testing-and-learning and scaling up the recycled plastic content in our petfood packs. As part of our Sustainable in a Generation plan, we are committed to doing our part to help drive a circular economy, which includes redesigning our packages for circularity. The fact that we are now able to introduce recycled content into our Sheba pouches helps us accelerate our journey to achieve 30 % average recycled content in our plastic packaging and to reduce by 25 % our use of virgin plastic" says Barry Parkin, Chief Procurement and Sustainability Officer at Mars.

Huhtamaki uses the certified circular polymer as a phthalate-free and gel-controlled film layer, which lends the flexible pouches high impact strength and puncture resistance even at low temperatures down to –20°C. For wet food packaging, the pouches must also be capable of withstanding a retort temperature of 135 °C for 60 minutes. Even higher thermal resistance of up to 160 °C may be needed in freezer-to-oven applications.

www.sabic.com

In the future, Sheba wet cat food will be sold in retort pouches with recycled content.