Innovative MultiNanoLayer Films

Recyclable Food Packaging

Recyclable MultiNanoLayer (MNL) films offer a sustainable alternative to traditional multi-layer packaging films. By reducing compatibilizer concentration and employing a continuous coextrusion process, these films can feature up to 1000 layers. The structure of the nanolayers influences the barrier and mechanical properties of these films.

View into the IPC technical center: Production of the MultiNanolayer film is running on the pilot line.
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Multilayer plastic films are widely used in food packaging due to their excellent barrier properties, which protect goods from contamination and extend their shelf life. These films consist of multiple high-performance layers, each serving a specific function. The outer layer provides sealability, printability, and abrasion resistance, typically made from polyolefins such as low-density polyethylene (LDPE), polypropylene (PP), high-density polyethylene (HDPE), and polyethylene terephthalate (PET). The inner layer offers oxygen barrier properties, with common materials including polyamide (PA) and ethylene-vinyl alcohol copolymer (EVOH) [1] [2].

A common design for these films is a five-layer film, where the central layer is surrounded by adhesive layers to bond with the outer and inner layers. This structure is used with barrier films containing PA or EVOH, which require copolymers as tie-layers to enhance adhesion due to their poor compatibility with the main structure polymers.

Despite their advantages, current multilayer films can face significant recycling challenges due to their complex design, which involves multiple polymers and structures. Materials such as EVOH and PA can contaminate the existing recycling streams and reduce their quality. However, the use of compatibilizers can help address some of these issues. Despite this, the current lack of effective sorting and recycling technologies further hinders their recyclability today.

The EU-funded Surpass project aims to evaluate the feasibility of developing MultiNanoLayer (MNL) polymer-based films using a specific coextrusion technology. This nanolayer processing technique uses a classic two- to five-layered feedblock combined with sequential layer multiplication dies. In this process, the polymer melt initially flows through

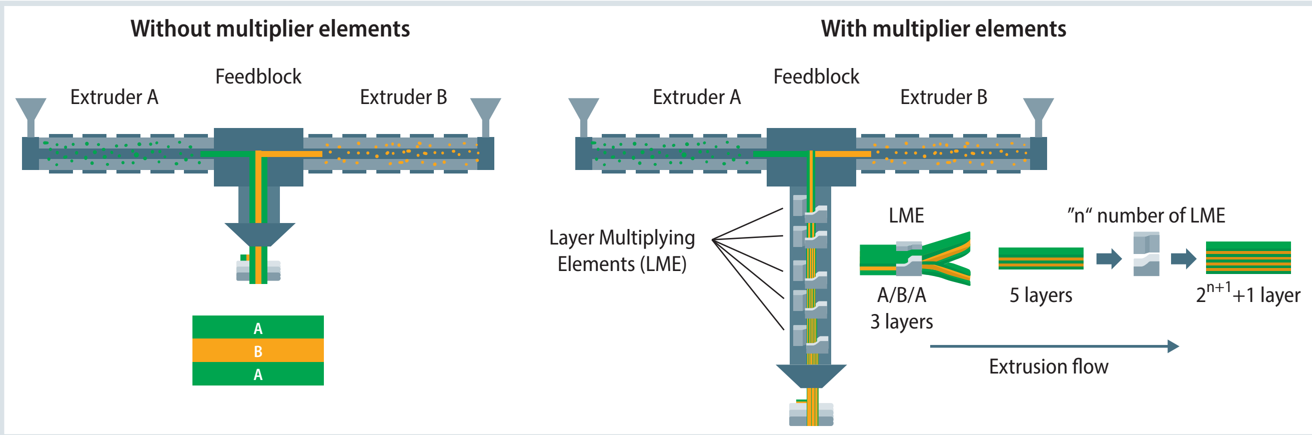

Fig. 1. Schematic illustration of the cast coextrusion process of the A/B/A multilayer coextrusion setup, where A= external layers (PE+compatibilizer) and B= barrier layer: a) without multiplier elements; b) with multiplier elements. Source: IPC, Innovation Plasturgie Composites; graphic: © Hanser

the feedblock and is then directed through a series of multiplier elements.

Smart Solution: the Melt Stream Is Fold and Stacked

These multiplier elements double the number of layers by cutting, spreading, and stacking the layered melt stream. The final number of layers in the polymer film depends on the number of layer multiplier elements used between the feedblock and the film or sheet exit dies [3]. The total layers in the resulting film can be calculated based on the initial layers in the feedblock and the number of multiplication dies (**Fig. 1**).

Nano-structuring using this technology allows the creation of films with excellent barrier, mechanical, and optical properties without the need for compatibilizing agents and reduces the costs. The effects on recyclability are currently being studied.

Multilayer films were fabricated using the coextrusion setup displayed in **Figure 1** with an exit die of 750 mm. Films with a thickness of 200 ± 50 µm were obtained.

For the first coextrusion trials, IPC implemented an A/B/A multilayer configuration, where "A" and "B" correspond to the externals and barrier layer, respectively. Regarding the material's selection, combinations of PE/EVOH were chosen as starting point. The polyethylene (PE) was used as external layers, the copolymer ethylene vinyl alcohol (EVOH) as the internal layers providing the barrier properties, and a polyethylene grafted with maleic-anhydride

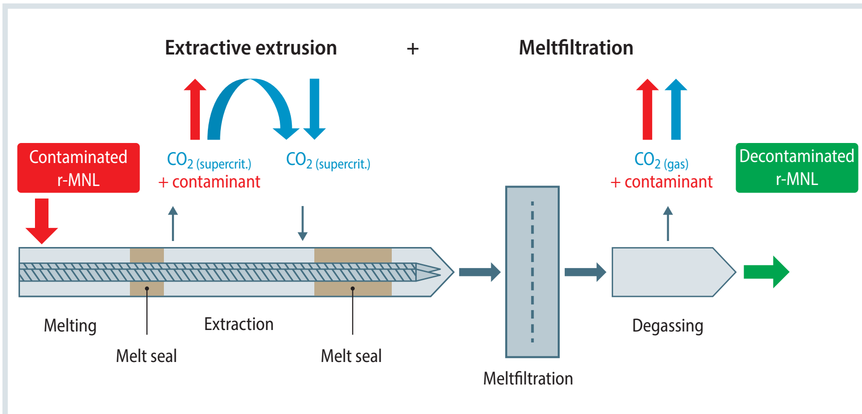

Fig. 2. Illustration of the Surpass decontamination process. Sourced: Fraunhofer ICT; graphic: © Hanser

(PE-g-ma) was used as a compatibilizer to improve the adhesion between the internal and the external layers. Films with and without compatibilizers were produced, featuring 17 and 65 layers, which correspond to the use of three and five layer multiplication dies, respectively.

Subsequently, a series of characterization techniques were employed to evaluate the final properties of films produced using the MultiNanoLayer process. These techniques included: a) barrier properties: oxygen transmission rate (ASTM D3985); b) optical properties: transmission, haze, and clarity (ISO 13468 (06–2019)); and c) mechanical properties: tensile test (ISO 527–3/2).

MultiNanoLayer Film's Performance

For PE/EVOH multilayers without compatibilizers, increasing the number of layers from 3 to 65 positively impacted the mechanical properties, slightly enhancing the elongation at break in the machine direction. The 65-layer film demonstrated an oxygen transmission rate (OTR) of 2.46 ml/(m^2·day). However, the transparency of the films decreased significantly, with see-through clarity dropping from 97 % for the 3-layer film to 36 % for the 65-layer film.

In contrast, 65-layer films with compatibilizers did not meet the Surpass project's OTR criteria of 10 ml/(m^2·day), regardless of the viscosity and flow rate ratio. Additionally, the presence of compatibilizers negatively affected both tensile strength and elongation at break properties.

In summary, we can conclude that, without compatibilizers, the multilayer system relies only on physical confinement, which makes the morphology control more challenging. In contrast, when compatibilizers are used, the system also depends on the chemical interactions between components in addition to the confinement effect. However, if the compatibilizer is poorly dis- »

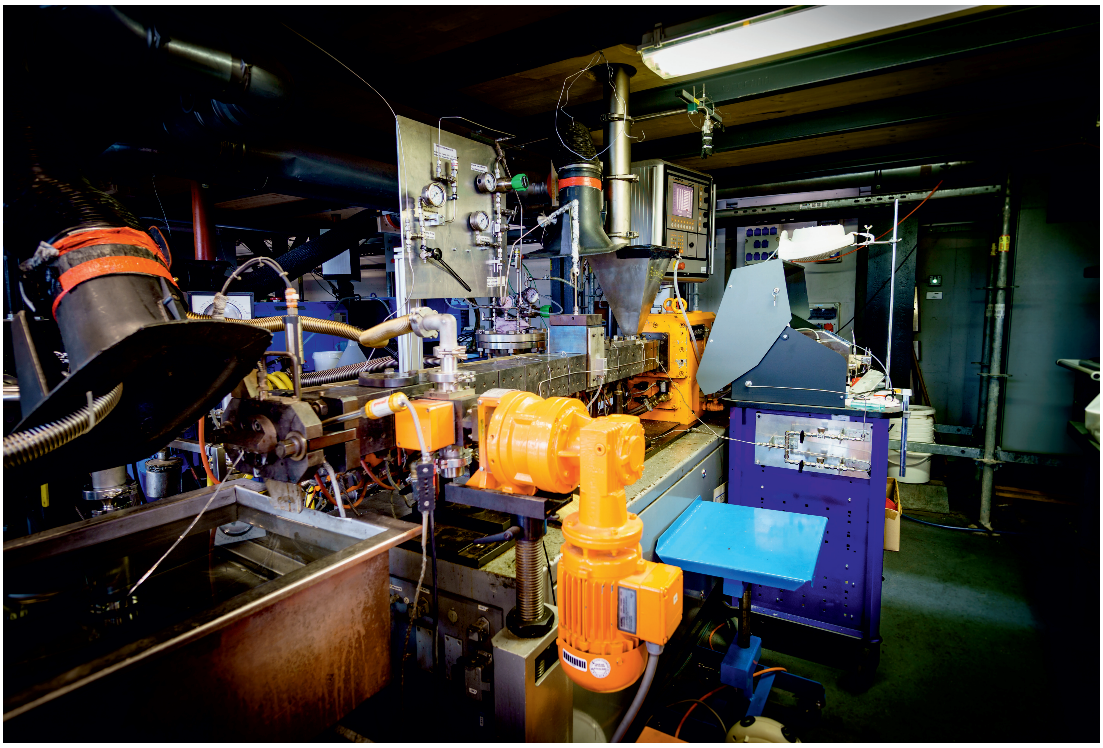

Fig. 3. Extractive extrusion pilot line at Fraunhofer ICT

persed, it results in weak adhesion and poor barrier properties.

Additionally, regarding the multilayer structure, increasing the number of layers can improve confinement and adhesion, thus enhancing barrier properties. But this is limited, beyond a certain number of layers, the barrier properties may deteriorate irrespective of the system's formulation or structural design.

Extractive Extrusion with Supercritical Carbon Dioxide

When packaging materials enter their end-of-life, they contain contaminants from various sources, including from their original production (additives in the material recipe), the goods which they protected and the processes they have undergone (thermal degradation, compounding with processing aids, film processing, packaging processing). These contaminants not only limit the material's reuse as a recyclate in new applications, they can also be harmful. They must therefore be removed.

In the Surpass project, films are purified in two process steps, both of which exploit the benefits of supercritical CO_2. The first step is decontamination via extractive extrusion and the second step is melt filtration.

Green solvents like supercritical CO_2 are already used at industrial scale, for example in the extraction of flavors from herbs. By adjusting the temperature and pressure, supercritical CO_2 can be used to dissolve a specific material. The majority of the processes are discontinuous and can be extremely effective, depending on the extraction time, temperature and CO_2 pressure.

However, the key disadvantage of discontinuous supercritical CO_2 extraction for high volume and comparably low-value material recycling (e.g. polymers) is the slow speed and high operational costs of the discontinuous processes. For the past few years, Fraunhofer ICT has therefore been working intensively to combine the efficiency of CO_2-based extraction processes with continuous processing on twin-screw extruders [for example in the EU-funded project "CREAToR" [4]. The main challenge is that effective extraction conditions – which can differ from one polymer/contamination combination to another, and which are typically easy to achieve in batch extraction – must be recreated in continuously operating twin-screw extruders.

Supercritical CO_2 ($scCO_2$) also shows exceptional behavior as a processing aid. It lowers the viscosity and the surface

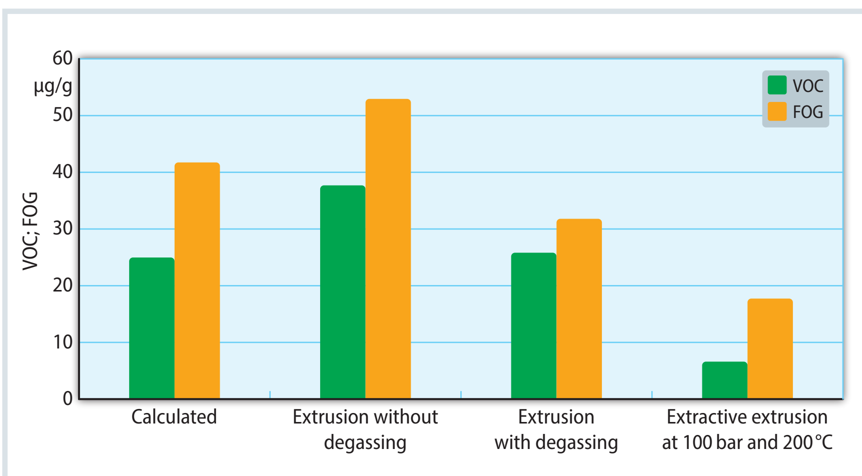

Fig. 4. Extractive extrusion of the virgin MNL material. Source: Fraunhofer ICT; graphic: © Hanser

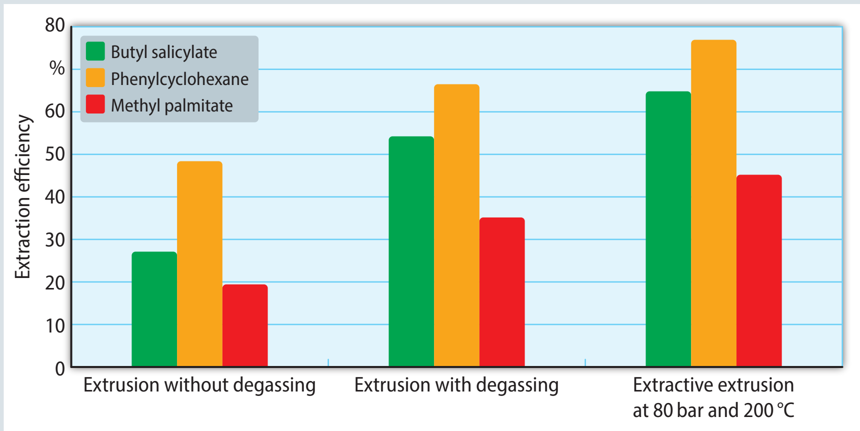

Fig. 5. Extractive extrusion of artificial contaminants. Source: Fraunhofer ICT; graphic: © Hanser

tension of the polymer mix during its processing. This is advantageous during a melt filtration process, enabling the use of lower mesh sizes or higher throughputs, resulting in better recyclate quality and lower energy consumption [5–8].

Pilot Line for Extractive Extrusion

Figure 2 outlines the process developed in the Surpass project, consisting of extractive extrusion and melt filtration steps. **Figure 3** shows the corresponding extractive extrusion pilot line at Fraunhofer ICT.

The contaminated MNL material is fed into the extruder and melted. The CO_2 is injected in a supercritical state in a counterflow to the melt-stream. The CO_2 with the dissolved contaminants leaves the extruder still in a supercritical state, the contaminant is separated, and the CO_2 can be recycled. The melt is then fed into the melt filtration device where any remaining solid residues are filtered. After the filtration step the polymer is degassed and the decontaminated recycled MNL is pelletized for its reuse.

Surpass first examined the extraction of contaminants from the virgin material recipe as described above..

Extraction Efficiency

Figure 4 shows the VOC and FOG analysis (VDA 278) of the polymer after extraction. The VOC and FOG amount increase compared to the virgin material as soon as the material is processed. This is due to the thermal degradation that always takes place during the thermal processing of a polymer. However, degassing decreases the content of volatiles, which exit the process line with the exhaust gases (without degassing vs. degassing). Further extraction with $scCO_2$ shows a further decrease of the VOC and FOG (degassing vs. extractive extrusion).

To evaluate the limits of the extraction efficiency, in a subsequent step the removal of artificially added contaminants was investigated. Three substances were chosen based on their solubility in supercritical CO_2 and their volatility: butylsalicilate and phenylcyclohexane are soluble and methylpalmitate is insoluble in supercritical CO_2.

All three artificial contaminants were removed from the polymer in the process outlined above. The extractive extrusion enhanced the removal compared to extrusion with degassing. **Figure 5** shows the extraction efficiency, the percentage of contaminant extracted. The contaminants soluble in supercritical CO_2 are removed according to their molecular weight: as the lighter molecule, the phenylcyclohexane is removed most effectively (up to 78 %). Furthermore the non-soluble methylpalmitate, which was not expected to be removed, was removed up to 45 %. This is likely due to a stripping effect.

The melt filtration with supercritical CO_2 is an ongoing task in Surpass. Initial results are expected by the end of 2024.

The supercritical CO_2 has shown its feasibility and, moreover, advantages in the recycling of MNL films. It allows the removal of various substances, even substances that do not dissolve in it, and it lowers the viscosity of the polymer enabling better processability. ■

Info

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References

You can find the list of references at ***www.plasticsinsights.com/archive***