PET: From A to C

Upcycling of Mixed APET Bottle Flakes into Thermally Stable rCPET Food Trays

Enhancing mixed bottle flakes by turning them into extrudable recycled crystalline polyethylene terephthalate (rCPET) was the goal of a joint development project looking to close the gap in the PET recycling system. By successfully producing a sheet made from recycled material suitable for high-quality applications such as thermoformed food trays, Gneuss, Sukano and Illig have demonstrated that this approach is indeed possible.

Thermally stable rCPET food trays made from multicolor APET bottle flakes (© Illig)

The recycling of bottle flakes derived from PET bottle collection systems as implemented and practiced in Germany, Austria and Switzerland, for example, has so far focused mainly on transparent and monochrome PET flakes. These can be recycled relatively easily into transparent food packaging. However, multicolored PET flakes (**Title figure**) are suitable only for inferior applications, because they cannot be re-palletized and extruded as reproducible homogenous PET due to their different colors. As a result, in the first quarter of 2019 in Germany, for example, multicolored PET flakes had a market value (500 to 700 EUR/t) of roughly only half of that of transparent PET pallets made from virgin material (1100 EUR/t) or recycled transparent PET pallets (1300 EUR/t).

Taking advantage of this cost benefit was what brought together Gneuss Kunststofftechnik, Sukano, the Swiss additive manufacturer, and Illig Maschinenbau, the manufacturer of thermoforming systems for thermoplastics, to collaborate on a joint development project. As initial test results show, the treatment of APET waste materials can close a gap in the current recycling system. The project demonstrated that it is possible to enhance a mixture of APET bottle flakes – that up till now has had only a marginal reusable value – to make reproducible, thermally stable rCPET (**see Info Box p. 43**), which can be extruded and re-formed into food-grade packaging in a thermoforming process (**Fig. 1**).

A further consideration in the project planning was the discussion about the migration of potentially hazardous substances found in aluminum food trays. Thermoformed and oven-safe food trays made out of recycled materials could be a good alternative. A further advantage of thermoforming in this process is the cost-effective production of high volumes of thin-walled, and thus resource friendly, thermoformed parts that can be made in a short time.

Homogeneous Melt with MRS Extrusion

Colored APET bottle flake is characterized by wide variations in color, molecular weight and contamination levels, due to their previous lifecycle. This is where MRS technology (MRS = multi rotation ex- »

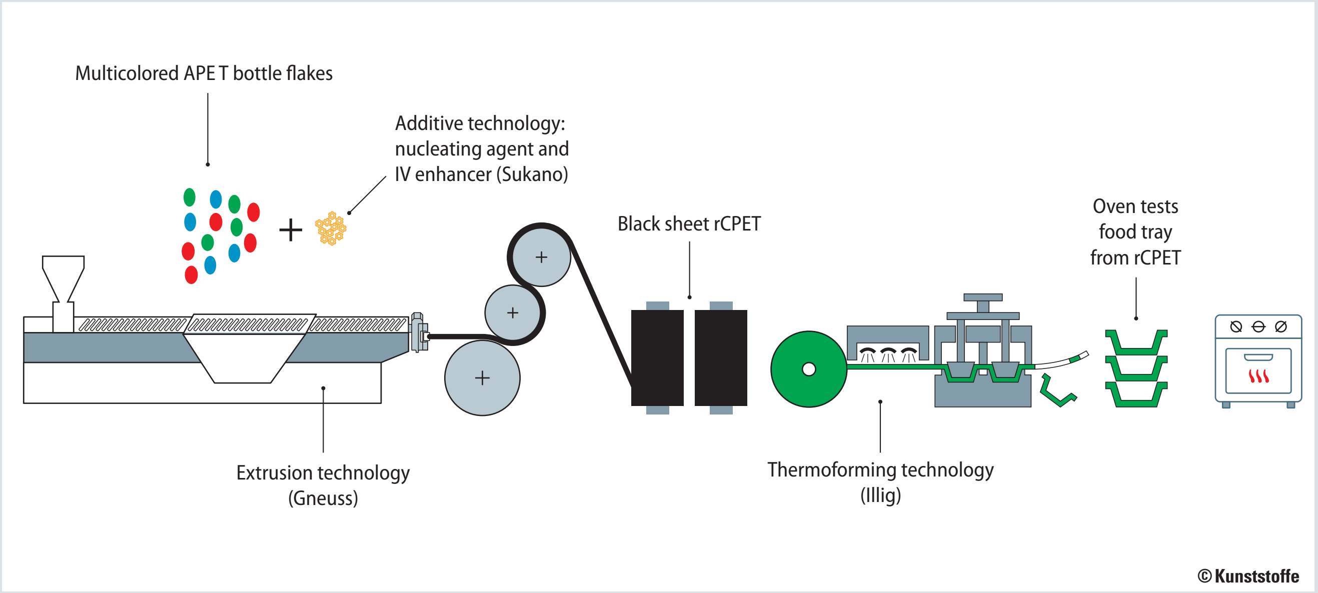

Fig. 1. Process overview: from multicolor APET bottle flakes to CPET for oven-safe food trays (source: Illig, Gneuss)

truder) comes in. In a single-screw extruder with a special degassing zone and satellite screws arranged around the main screw, there is a continuous exchange of material between the satellite screws at moderate vacuum conditions of 25 mbar (**Fig. 2**). Thanks to the rapid, continuous surface exchange between the main screw and the satellite screws under vacuum, the surface exchange of the polymer melt is greatly increased, which allows for an extremely efficient devolatilization and decontamination of the polymer melt (**Fig. 3**).

The polymer melt is homogenized, providing excellent material sheet properties for thermoforming in a later step thanks to the very evenly and consistent molecular weight distribution. Moreover, the extremely efficient mixing process in the MRS section facilitates the even distribution of additives such as a nucleating agent into the polymer melt. This procedure of equally distributing the additive into the material also has the added benefit that the crystallization of the material sheet in the downstream thermoforming process is consistent throughout and can thus be predictably controlled.

Because the MRS concept makes it possible to avoid thermal preconditioning of the material prior to extrusion and thus eliminates the otherwise typical thermal stress caused by crystallization and drying, the process chain during the processing of the polymer is very short. The polymer melt is processed gently, preserving excellent physical and visual properties like high tensile strength and impact resistance, transparency and a low yellowness index rating (in the case of transparent sheets).

Not only the extruder itself, but also melt filtration is of particular importance for the sheet quality when processing rPET. That is why the Gneuss sheet line includes a process-constant, fully automatic backflush filtration system. The RSFgenius rotary filtration system reliably and efficiently removes contaminants such as solid particles from the polymer melt. For permanent process monitoring, an online viscometer measures the viscosity and thus serves as a quality-assurance instrument (**Fig. 4**).

Downstream from the MRS extruder unit, an rCPET sheet can be produced on a sheet extrusion line and used connected directly to an inline thermoforming machine or wound up on a roll for later offline use.

Fig. 2.. Multi rotation extruder system with satellite screws arranged around main screw (© Gneuss)

Additives for Color and Crystallization

The properties of the PET bottle flake material is intentionally modified in the extruder by introducing additives. The rPET IV enhancer from Sukano elongates the molecular chain of the polymer and by doing so increases the molecular weight (**Fig. 5**).

The additive also improves the melt viscosity, which also benefits the processing of the plastic at a later stage. As for the sheet extrusion, the additive extends the processing window, increases processing speed, and improves the material sheet quality. Moreover, the additive ensures a higher impact resistance of the plastic.

With this treatment, PET is comparable to virgin APET in its physical properties, with the disadvantage of its non-transparency. Because of this, it is not suitable for transparent packaging. However, an oven-safe rCPET tray is

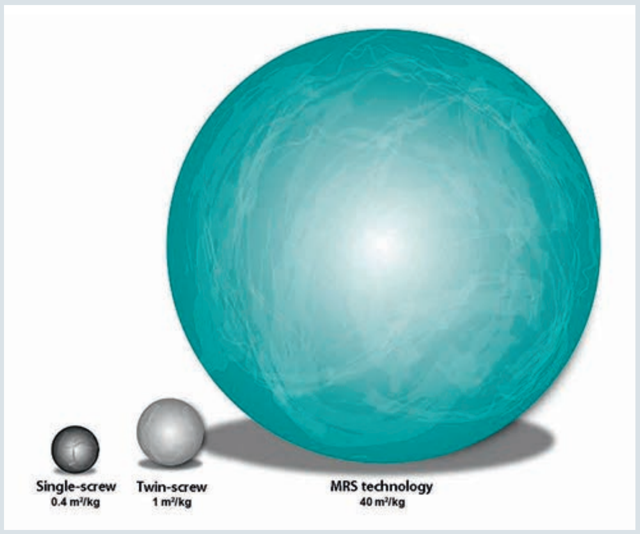

Fig. 3. Surface renewal for the decontamination of plastics: the MRS technology is 100 times more effective than conventional single-screw technology thanks to its satellite screws (© Gneuss)

normally opaque due to its high concentration of crystallites. Because of this, it makes sense to color the rAPET prepared in the MRS extruder with a masterbatch and to transform it into a sheet suitable for thermoforming using a crystallization agent. Sukano uses its own rPET crystallization masterbatch, which obtains good color results with thermally stable color pigments.

Sukano develops nearly every color the market demands. However, the most typical colors are white, beige and black. Black is a typical color used in rCPET trays, which is also the most widely used color in the production of CPET trays made of virgin material. A radar-camera sorting system developed by Fraunhofer researchers and dubbed "BlackValue" can identify and sort black rCPET and CPET food trays, as well as all other colored plastics, in real time and in large quantities in the stream of falling flakes [1].

The nucleating agent accelerates the crystallization rate of the plastic, making the formed rCPET trays oven-safe: their form remains stable for at least 20 min at 200 °C. Moreover, the nucleating agent is also key in the latter stages of the production chain in controlling the crystallization process during thermoforming, which improves the production stability of thermoforming the trays.

rCPET Food Trays

Gneuss MRS extrusion technology meets the requirements of various food safety regulators worldwide including the FDA, EFSA, Invima, Senasa, Anvisa for hotfill applications, and for room temperature storage. Similarly, Sukano's rPET additives are suitable for food-grade polymers, ensuring that an rCPET monofilm is well-suited for packaging that has direct contact with foods.

Due to the increased migration at higher microwave and oven temperatures, the sheets used to form rCPET food trays are generally made with a co-extruded functional barrier of virgin materials for protection against contaminants in the sheet. Equally, in the final stages of the production of food trays, the thermoforming systems from Illig also comply with strict hygiene requirements with their integrated cleantivity concept for hygienically clean production.

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Material roll number	Percentage of multicolor APET bottle flakes	Black nucleating agent	IV enhancer	IV [dl/g]
1	100 % (control sample)	–	–	0.70
2	95.0 %	5 %	–	0.69
3	93.0 %	7 %	–	0.72
4	92.5 %	7 %	0.5 %	0.73
5	92.0 %	7 %	1 %	0.83

Table 1. Material rolls with different additives (source: Illig)

Amorphous and Crystalline PET

Polyethylene terephthalate (PET) collected from used bottles that have been shredded into bottle flakes is used as the initial raw material. Generally, a distinction is made between amorphous (APET) and crystalline polyethylene terephthalate (CPET). APET is known for its high transparency, while CPET has the advantage of being heat resistant, a property that enables formed parts (e.g. thermoformed food trays) to withstand oven temperatures of up to 200 °C without deforming under the heat.

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Extrusion of the Sample Sheets with Different Additives

For the joint series of tests, Gneuss first produced a sheet without additives as a control sample from a batch of APET bottle flakes. This was followed by four further monofilms, which had different additive concentrations through gravimetric dosing (device type: Guardian, gravimetric batch blender for 6 components; manufacturer: Processcontrol, headquarters Birstein, Germany). All five sheets were 530 mm wide and 0.5 mm thick.

An online viscometer monitored the melt viscosity during sheet extrusion, which as expected increased with the addition of the IV enhancer (**Table 1**). However, the increase in intrinsic viscosity (IV) was less pronounced for sheet 4 compared to sheet 3 at 0.01 dl/g, while a further increase in IV enhancer dosage by the same amount increased the intrinsic viscosity by 0.10 dl/g to 0.83 dl/g (sheet 5). Future testing needs to be conducted to explain the unexpected low effect of the low dosage.

Process-Controlled Thermoforming Technology

For the production of trays, a multi-dimensional radiant heater is required like the one employed by Illig in the tunnel heaters of their thermoforming machines. This is necessary because the crystallization of PET sheet can only be controlled by precision zonal temperature control in both the lateral and longitudinal directions. The tool technology is also designed specifically for the PET process as a two-step forming tool with heated cavity walls ($T_g < T_{\text{tool cavity wall}} < T_s$) in the first forming tool and cooled cavity walls in the second tool ($T_{\text{tool cavity wall}} < T_g$), where T_g stands for glass transition temperature and T_s for crystallite melting temperature of PET. In the first stage, the tray is given its form, receiving thermal energy for sufficient crystallization through contact with the heated tool cavity walls. The tool opens and the preformed ductile trays are moved along by the material transport into the second cavity with cooled tool cavity walls. The tool closes and in the second forming step the plastic hardens under contact with the cooled tool cavity walls, maintaining its shape while the crystallization process is completed – the formed trays are now oven-safe.

Material roll number	245 °C	250 °C	260 °C	270 °C	280 °C	290 °C
1		–	–	Good	–	–
2	Good	Good	Good	Sufficient	Sufficient	Poor
3	–*	Good	Good	Sufficient	Sufficient	Poor
4	Good	Good	Very good	Sufficient	Sufficient	Poor
5	Sufficient	Poor	Poor	Poor	Poor	Poor

*– Trays not formed * Propensity of material sheet to stick is too high*

Table 2. Forming accuracy for the thermoforming tests of the sample material rolls (control sample and rCPET) at different temperatures of upper and lower heaters (OHZ/UHZ) (source: Illig)

Striking a Balance between Forming Accuracy and Thermal Stability

From the five material sheet types, Illig produced food trays on their IC-RDK 80 thermoforming machine using an internal test tool with 2 + 2 cavities. During the entire series of tests, the first tool cavity of the two-step forming process was heated to 160 °C and the second tool cavity was temperature-controlled to 20 °C. The only exception was for material roll 1, the sample material roll made of 100 % bottle flakes, for which the forming tools were temperature-controlled to 20 °C. The temperature setting of the upper and lower heating in the machine varied from 245 to 290 °C. All other process parameters remained constant.

The level of definition of the formed trays served as an important quality indicator as measured by the visible impressions made by the vacuum holes on the surface of the formed trays. In contrast to thermoforming rAPET, when thermoforming rCPET the forming accuracy decreases in proportion to the amount of heat added. This is because increased crystallinity increases the viscosity of the material sheet. This means, a well-defined formed tray can be an indicator for a low level of crystallization and thus for poor thermal stability of the formed part. When applying an additive in the manufacturing of a material sheet for the purpose of forming rCPET food trays, it is therefore essential to strike a healthy balance between an acceptable degree of forming accuracy and thermal stability.

Table 2 clearly shows that there are hardly any differences between the material rolls 2, 3 and also 4 in terms of their definition. From an upper and lower heater temperature of 270 °C, the onset of crystallization seems to reduce the definition of the formed part. The rCPET food trays from material roll 5 are not well defined at the selected temperatures. With

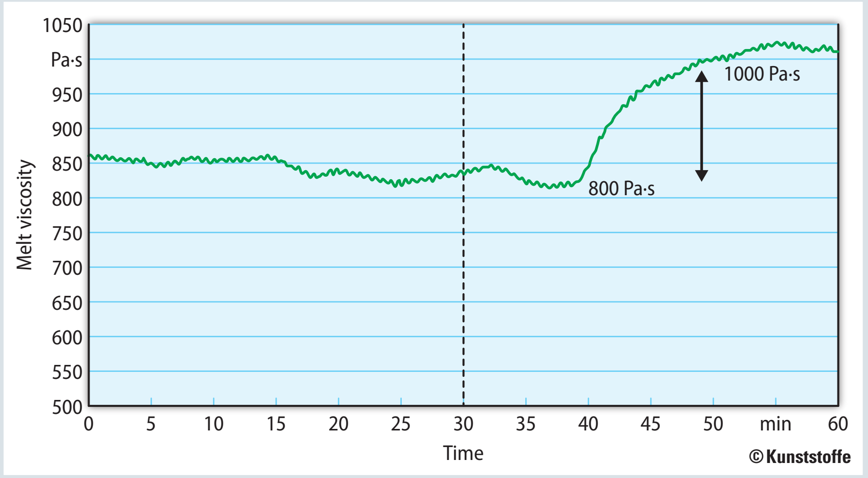

Fig. 4. The timeline of the dynamic melt viscosity shows an increase from around 800 to 1000 Pa·s as a result of the addition of 1 % rPET IV enhancer (source: Gneuss)

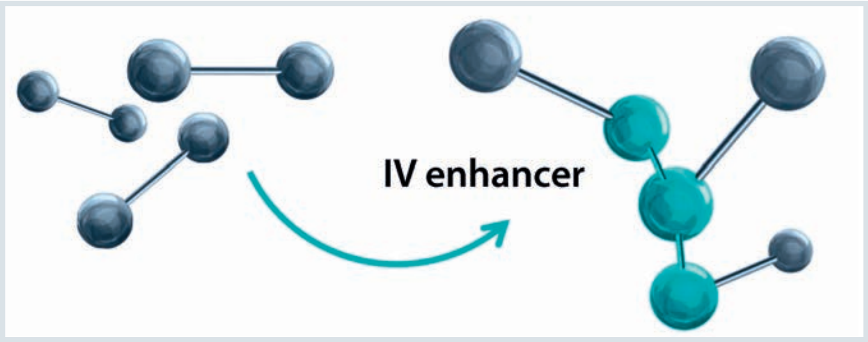

Fig. 5. Chain-growth polymerization mechanism using the rPET IV enhancer (© Sukano)

92 % PET bottle flakes, test roll 5 has the lowest percentage of raw PET compared to the nucleating agent.

Oven Tests in Packaging Lab

The oven tests at 200 °C for 20 min were carried out in Illig's packaging lab. One oven test was conducted immediately after thermoforming and a second test was carried out after an 18-hour storage of the formed food trays at a room temperature of 22 °C to determine the influence, if any, of a possible post-crystallization. This proved however to be negligible, as no differences were detected.

The thermoformed food trays from the sample material sheet (APET without additives) were as expected not thermally stable, so that no visual evaluation was possible. The comparison of food trays formed from the sheets with additives showed that at a temperature of 270 °C of both the upper and lower heaters, all food trays had a high dimensional stability. The food trays formed from material roll 5 were matt in appearance, which can be explained by having the highest concentration of the nucleating agent (**Fig. 6**).

Apparently, as the percentage of nucleating agent increases, so does the thermal stability of the food trays. This effect is especially noticeable at a temperature of 270 °C of both upper and lower heaters (**Fig. 7**).

In Conclusion: Potential for High-Quality Applications

Depending on customer requirements, a concentration of 5 % of the nucleating agent from Sukano may already be sufficient to obtain high-quality oven-safe rCPET food trays from previously low-value APET bottle flakes. Moreover, as the percentage of rPET-IV enhancer increases, so does the food tray's impact resistance, which shows potential for high-quality applications of thermoformed rCPET containers in the refrigeration and deep-freeze sector.

With the growing demand for recycled pellets, in order to meet minimum recycled content requirements in the final products, the availability of transparent recycled PET is becoming increasingly scarce. One industry that makes use of multicolor PET flakes is the strapping industry, turning the PET flakes into packaging strapping. One of the reasons multicolored PET flakes are used for this purpose is because there are no restrictions in terms of food safety regulations. There is a surplus of multicolored PET bottle flakes on the market, but currently they are utilized only in a limited capacity. The joint development project considered economic, legislative and technical requirements and demonstrated that the recycling of multicolored APET blends into new high-quality products is indeed possible.

Upcycling instead of downcycling – upgrading the recycled plastic into food-grade rCPET is technically easy to implement and fills a gap in the PET recycling system. Thermally stable rCPET food trays as a high-quality final product are only one of many possible applications. ■

Fig. 6. Oven tests at 200 °C for 20 min: rCPET trays (from left to right: rolls 2, 3, 4, 5); upper heater at 250 °C; upper and lower heating, lower heater at 270 °C (© Illig)

Fig. 7. rCPET food trays made from material sheet 5 before and after the oven test at 270 °C on upper and lower heater (© Illig)