Abstract.
The consumption of PET has grown for many years. This growth is being accompanied by a mounting volume of reclaim material of different origin. Most of the scrap produced during processing is treated and recycled in-house, but large quantities of washed, sorted regrind material are also coming out of the consumer cycle, and are being traded as recycled for subsequent processing. Even with virgin material, pre-drying is of eminent importance in the conventional processing of PET on single screw extruders. PET is hygroscopic and very quickly absorbs the equilibrium moisture of 1000-3000 ppm of water (depending on the particular product). But preparation of the material is even more complex in case of recycled material. It has to be agglomerated, crystallized and pre-dried before extrusion and, apart from that, it also has to be sorted according to its intrinsic viscosity (IV), which differentiates one material from another. It is the IV that determines which field of application the PET recycled can be used for (0.4-0.65 textile fibers, 0.75-0.95 bottles…). For the preparation and extrusion of PET, Coperion Werner & Pfleiderer has developed a technology which eliminates not only the pre-drying of the recycled, but also the crystallizing and the agglomerating process.

Introduction

Even using virgin material, the pre-drying step is of great importance in the PET processing in the conventional single screw extruders. The PET is hygroscopic and absorbs humidity until the equilibrium of 1000-3000 ppm depending on the particular product. The preparation of the material still is more complex in the recycling case. The material has to be accumulated, pre-crystallized and pre-dried before the extrusion, and moreover, it has to be separate according its intrinsic viscosity, that differentiates a material from the other. It is the IV that determines the field of application of the recycled PET: (0.4 - 0.65 dl/g for textile staple fibers, 0.75 - 0.95 dl/g for bottles, etc). For the preparation and processing of PET, Coperion Werner & Pfleiderer has developed a technology that not only eliminates the pre-drying of the material to be recycled, but also the pre-crystallization and the process of agglomeration. Through some tests, it was verified that thanks to the characteristics of the corotating twin screw extruder, it is possible to process the PET with low loss of intrinsic viscosity. The only requirement of the process is in relation to the contamination limits. The material can contain in maximum 50 ppm of PVC and 50 ppm of polyolefin, because these materials degrade at the temperature of 270-280 °C, that it is necessary to melt the PET. Mainly the PVC causes a more intense degradation in the PET. The direct extrusion process is based on a processing of low degradation and an efficient degassing in the twin screw extruder (ZSK Mega Compounder). This technology is applied in such a way for processing of virgin material, as of recycled material, being able to produce granulated films, staple fibers or for injection. As main advantages, we have:
- The energy and time savings, because there is no need for pre-drying or crystallization.
- The very high quality of the end product, because there is only a minimum decrease in the IV during processing and because glass-clear material has a much lower yellow cast than with process involving pre-drying.
- The high flexibility, because, due to the self-cleaning characteristics of the twin screws, changing a formulation and colors takes less than 30 minutes.
- The much simplified logistics, because granulated virgin material and different reclaim material (regrind, agglomerate, flakes) can be processed together even if different IV.

Experimental

Influence of the Moisture

While plastifying humid product, hydrolytic degradation will immediately start, being 10.000 times faster than thermal degradation caused by too high processing temperatures and being 5.000 times faster than thermo-oxidative degradation caused by the presence of oxygen. So the removal of retained moisture is the main problem for the processing and compounding of PET. There are several possibilities for setting low process moisture content:
- Standard-crystallisation at 150°C and drying at 150–180°C
- Air-drying process at temperatures of max. 60 °C without crystallisation

The Polymer Processing Society 23rd Annual Meeting
• Combination of pre-drying or conditioning and vacuum degassing
• Vacuum degassing at extrusion

The preparation of the material is even more complex in the case of recycled material. It has to be agglomerated, crystallised and predried before extrusion and, apart from that, it also has to be sorted according to its intrinsic viscosity (iV), which differentiates one material from another. It is the iV that governs which field of application the PET recycled can be used in.

<table>
<thead>
<tr>
<th>Viscosity</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,85 – 1,5  dl/g</td>
<td>Monofilaments, Technical yarns, High-strength packing straps</td>
</tr>
<tr>
<td>0,80 – 0,84 dl/g</td>
<td>Bottles for food (Mineral water, Softdrinks, Beer) and other non-food applications</td>
</tr>
<tr>
<td>0,68 – 0,76 dl/g</td>
<td>A-PET-Films and Sheets for Thermoforming</td>
</tr>
<tr>
<td>ca. 0,6 dl/g</td>
<td>Bi-axial oriented films</td>
</tr>
<tr>
<td>0,58 – 0,62 dl/g</td>
<td>Staple fibres (Chopped fibres), Filling fibres, Carpet fibres, Spin bonded fabric</td>
</tr>
<tr>
<td>0,60 – 0,80 dl/g</td>
<td>Reinforced materials, Polymer blends</td>
</tr>
</tbody>
</table>

Viscosity           Application
0.85 – 1.5  dl/g Monofilaments, Technical yarns, High-strength packing straps
0.80 – 0.84 dl/g Bottles for food (Mineral water, Softdrinks, Beer) and other non-food applications
0.68 – 0.76 dl/g A-PET-Films and Sheets for Thermoforming
ca. 0.6 dl/g      Bi-axial oriented films
0.58 – 0.62 dl/g  Staple fibres (Chopped fibres), Filling fibres, Carpet fibres, Spin bonded fabric
0.60 – 0.80 dl/g  Reinforced materials, Polymer blends

Over the years, the process engineering has been constantly refined and adapted to the needs of the market. This direct process is based on the good processing properties and the high venting efficiency of the twin screw compounder (grade: ZSK MEGAcompounder PLUS).

The technology is suitable for virgin material, for all kinds of regrind and recycled, and for blends of these materials, and it leads directly to film, fibres or injection moulding granules. Following table shows a comparison, drawn up externally, of the ZSK process, with various single screw processes. It highlights the min benefits of processing in a single step.

With the ZSK process, the throughput is limited neither by the pre-drying capacity nor by the screw size. For example, a ZSK McPLUS with a screw diameter of D = 92 mm achieves a throughput rate of 2000 kg/h. For this throughput at least a 200 mm single screw would be necessary in the case of a single screw unit and, because of the energy input through heat, conduction, non-molten areas can form.

100% virgin material, 100% reclaim material or mixtures of the two can be used in any ratio. The only requirement made on the reclaim material concerns its purity. It can contain a maximum of 50 ppm PVC and 50ppm Polyolefin, because these materials degrade at the melt temperature of 270-280°C that is needed for PET, with the result that decomposition products contaminate the PET and – especially in the case of PVC - cause more intense degradation of the PET. Fibre waste can also be used if it has been shredded in a compactor and condensed to produce a free-flowing, meter able bulk material.

The processing section of the compounding extruder comprises 8 barrel sections, each 4 D long, giving a total length of 32D.

The screw is designed with appropriate screw elements specifically for the particular function - melting, venting, homogenizing.

In the third barrel section, in other words immediately after commencement of the melting process, a large proportion of the water released during heating, escapes by atmospheric venting. Subsequently, a vacuum venting system with an absolute pressure of max 10 mbar extends over barrel sections 5-7. During this period, not only the residual moisture removed from the melt, but so are any low molecular weight components that are still present or have been newly generated through material decomposition.
The decisive factors for the good venting effect are, apart from the length of the venting zone, the large melt surface area through the partial filling and the constant changing of the surface due to intensive mixing. Because of the large free volume and the diameter ratio of $D_v/D_i = 1.55$, the ZSK MEGAcompounder PLUS is also very suitable in this respect.

To extract the gas, it is advisable to use a side venting system. With this design, no deposits from the vents can get back into the melt and contaminate it. The key role played by venting in the processing of PET comes from the fact that this plastic is produced by polycondensation, in other words through the splitting off of water.

**Results and Discussion**

Accordingly, at elevated temperatures and in the presence of water, the reverse reaction can take place, hydrolysis, which can break down the material. Because these are equilibrium reactions, the IV an thus the quality of the end product can be influenced solely by the choice of process conditions and without any addition whatsoever of coupling agents.
Generally speaking, a high mechanical stress on the melt and a poor venting system encourage the degradation process. The more accurate evaluation in Fig 1 shows that the lower the standard throughput, the lower the degradation. In concrete terms, this means that a long residence time and a low filling level produce a smaller reduction in the intrinsic viscosity and, in an extreme case, can even result in a slight increase.

When recycling bottle regrind for fibre production, it is possible, during processing, to specifically degrade the PET via suitable process parameters because the starting IV value of 0.78 to 0.8 dl/g of the bottle materials is much higher than the value needed for fibre material, namely approx. 0.6 dl/g.

The output section of the compounding and the downstream units must, of course, be suitably adapted for direct flat film extrusion. Because of the low melt viscosity of the PET, a gear pump is always used to build up the extrusion pressure. With its high efficiency in building up pressure, it makes an important contribution to keeping the melt temperature down. A subsequent filter with an automatic screen changer catches any remaining impurities. The fineness of the screen will depend on the specifications for the manufacture of the end production of fibres and biaxially oriented film. The filtered melt is extruded with a slit die or added to the subsequent spinning process via spinning pumps.

The concept described here is also suitable for multi-layer films as is shown by the successful operation of a film production line for the manufacture of a coextruded three-layer film at a well-known Danish packaging producer. The facility has a ZSK 92 Mc as main extruder and two ZSK 50 Mc’s a coextruders on one line, on the other line a ZSK 119 McPLUS with a ZSK 70 McPLUS a co-extruder. The prime reasons for choosing this concept were the energy-savings due to the elimination of the pre-drying process, the very short changeover time of only 30 minutes for a material of colour change, and the high mechanical and optical quality of the film.

Table below shows part of the results that had been achieved with different raw materials, different residual moisture contents and 5 mbar absolute vacuum pressure. It is obvious that materials of IV around 0.6 dl/g show rather no degradation whereas the higher viscous materials like the 9921W degrade about 0.03-0.04 dl/g. Only the bottle flakes with a comparable viscosity of 0.08 show a higher degradation at constant operating conditions.
To find out the reason for the difference between bottle flakes and virgin material one has to look at the sources.

### Conclusion

Due the combination of the high torque and the degassing, it is possible to process PET at a minimum intrinsic viscosity loss, but there are also other influences in the process such as selection of bottles from refillable bottles cycle, unsorted plastic waste from domestic, shop and industry, contamination with different polymers like PE, PVC, PA, PVAC, metals, glue and so on. Some of those contaminations can be separated in an appropriate melt filter, others like e.g. glue or sealing materials, foreign plastics and residual detergents from the washing process have a direct influence on the degradation of the PET, so a proper grinding and washing process is an important step to achieve high quality material. Although the PET doesn’t need to be predried, it is important that the inlet material doesn’t have more than 5000 ppm moisture, otherwise the degradation will take place and the IV loss will increase.
Higher the machine torque, lower is the degradation of the PET under the same running conditions. The ZSK MegaPlus with 20% more torque available is the most reliable machine to process the PET at a minimum iV loss. Normally we have limited the PET extrusion at 400 rpm screw speed to have a very gentle process and due the high free volume it is possible to remove big amounts of volaties.

Acknowledgements

I appreciate the efforts from Sabine Schönfeld and Frank Lechner from Coperion Werner & Pfleiderer with the development of this process.

References