ELIMINATION OF VOLATILE CONTAMINANTS IN RECYCLED PLASTICS

Vicent Martínez, Mechanical Recycling Group and extrusion expert

The European Union has recently implemented a circular economy action plan in which plastics are considered a key priority for addressing the challenges created by these materials throughout the value chain taking into account their entire life cycle. In particular, in January 2018, the European Commission published the European Strategy for Plastics in a Circular Economy[1]. The objectives set out in this communication are highly ambitious and include:

- By 2030, all plastic packaging placed on the EU market will either be reusable or recyclable., Ecodesign improvements will be applied and single-material structures will be promoted.
- Increase the overall European recycling industry capacity so that more than 50% of plastic waste is recycled by 2030.
- The demand for recycled plastics will be encouraged so that more and more products are made entirely of recycled plastic. The Circular Plastics Alliance[2] initiative estimates that around 10 million tonnes of recycled plastic will be used to manufacture new products by 2025.

Mechanical recycling is the most feasible and widely implemented process at European level to recover large quantities of recycled plastic material. This process generally involves shredding the plastic material and feed into an extruder, where it is melted and homogenized at high temperatures to obtain recycled pellets that can be transformed into new products by extrusion, injection moulding, rotomolding, etc.

The characteristics of the source material have a significant impact on the recycler's associated costs and performance. Cleaner, less contaminated plastic waste means lower pre-treatment costs and preliminary washes. However, post-consumer plastic waste may be accidentally contaminated due to different factors:

- Presence of impurities or retained substances.
- Improper use of packaging by filling with other products.
- Degradation due to heat, oxidation, UV radiation, hydrolysis, etc.
- Inadequate separation of materials.
- Cross-contamination during waste collection.

If the recycled thermoplastic pellets are very dark in colour or show traces of contaminants and a high content of volatile compounds that release unpleasant odours, their use is limited to low value-added products such as films for litter bags, micro-irrigation pipes, pots and street furniture. Many types of plastic products currently require complex recycling at the end of their life cycle, such as printed films, packaging holding contaminant products and plastic components

[1] https://ec.europa.eu/commission/publications/factsheets-european-strategy-plastics-circular-economy_en
[2] https://ec.europa.eu/growth/industry/policy/circular-plastics-alliance_en

containing halogenated flame-retardant additives. The aim is therefore to increase the efficiency of the mechanical recycling process by developing extrusion technologies that can extract volatile compounds and contaminant substances in thermoplastic materials.

Some extruder configurations are fitted with several vacuum degassing ports to eliminate residual monomers and oligomers in the purification of thermoplastic resins. Vacuum devolatilization has some limitations when eliminating substances with low vapour pressure, as well as substances that have interacted with the thermoplastic matrix, in which case, it is not possible to reduce contaminant substance levels below 500 ppm. Working at low production speeds and high vacuum levels frequently causes melt material to escape through the venting ports.

Adding liquids such as water and alcohol solutions in the extrusion process to act as stripping agents involves working with high-temperature profiles in the extruder so that the liquids evaporate in the form of bubbles that can be dispersed in the melt flow to form a kind of microfoam that increases the specific surface area and, therefore, the capacity for transfer and diffusion. High-temperature processing can increase the risk of degrading the thermoplastic matrix, which means that process parameters must be optimized and residence times carefully controlled. Most non-polar substances are insoluble in polar solvents such as water. When organic solvents are used, additional devolatilization and purification steps are necessary to ensure complete elimination of any residual solvents in the product.

A highly advantageous alternative to organic solvents involves extraction with supercritical fluids. A supercritical fluid is a substance whose pressure and temperature are above its critical point, which means it shows the properties of a fluid with high diffusivity (gas) and high dissolving power (liquid). This form of extraction is more efficient for substances with a low vapour pressure and compounds with a low molecular weight.

Carbon dioxide (CO_2) is one of the most common supercritical fluids and is known for its , low toxicity, high compatibility, low cost and immediate elimination. It is also non-flammable and non-corrosive.

In the transformation of thermoplastic materials, CO_2 in supercritical conditions has been added during extrusion as a process aid with plasticizing effect, a modification agent in tribological applications and an impregnation agent in colouring and dyeing processes of synthetic fibres[3]. This plasticizing effect reduces viscosity and shear stresses. It also helps prevent thermal degradation in polymers sensitive to high temperatures, as well as plastics that are highly viscous and those with a high filler content. It therefore enables transformers to reduce processing temperatures, which saves energy, reduces torque and head pressure, and improves filling flow in injection moulds and dies.

Carbon dioxide also show good compatibility with the polymer and a greater affinity for contaminant substances. Its good penetration and solubilization swells the polymer matrix (up to 20% for polypropylene), which favours contaminant diffusion. Decompression of CO_2 generates bubbles and a micro-foam that speeds up diffusion. However, the volatility of the contaminant ultimately determines elimination effectiveness.

AIMPLAS has implemented an extrusion technology for reprocessing thermoplastic materials that includes a continuous injection system for CO_2 in supercritical conditions to eliminate

[3] S.G. Kazarian *Polymer processing with supercritical fluids* Polymer Science Vol 42 No 1 2000

volatile substances, odours and other contaminants. The following picture shows the basic configuration of the process.

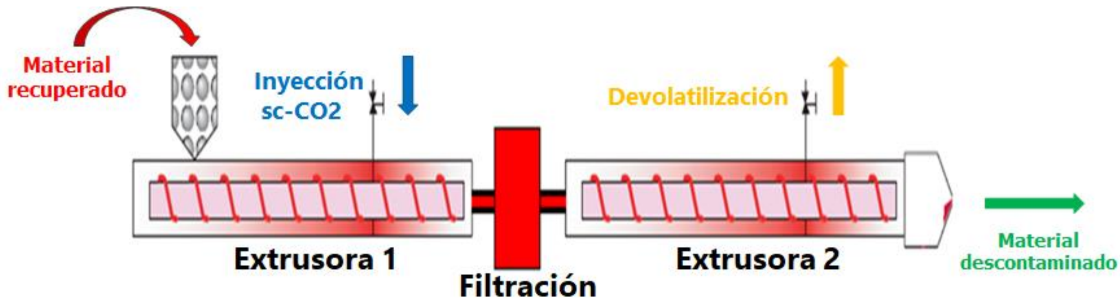

Figure 1. Diagram of the extrusion process with supercritical CO_2 injection.

This technology has been successfully used to recycle different products with the aim of improving the quality of the recycled plastic material by reducing its content of contaminant substances, volatile compounds and unpleasant odours.

This is the case of packaging contaminated with hazardous substances, such as high-density polyethylene (HDPE) drums and jerrycans used to transport industrial and phytosanitary solvents. At the end of their life cycle, this packaging is contaminated with these liquids, which can impregnate the inner surface of the packaging and can be absorbed by the material. Managing this kind of waste is complex and expensive and very few recyclers are able to recover contaminated packaging. Traditionally, these materials were recovered using different phases, which started with washing and shredding the drums and jerrycans. The shredded plastic material then went through different intensive washing and drying cycles before it could be extruded. Thanks to the use of this supercritical CO_2 injection technology in the mechanical recycling process, recycled plastic pellets are obtained after effective elimination of volatile compounds and contaminants. The number of phases prior to washing and drying is also reduced, thus resulting in savings on water and chemical agents.

Figure 2. Examples of HDPE containers for transporting solvents and phytosanitary products.

The other success story involves recycling low-density polyethylene (LDPE) films used to manufacture bags and other flexible packaging formats. This type of film usually has a printed layer of inks that create designs in different shapes and colours. The pellets obtained directly from this plastic are very dark in colour due to the mixture of pigments. Inks and varnishes also tend to thermally decompose during the high-temperature extrusion process and generate a large number of gases and volatile compounds, thus resulting in a poor-quality product with lower mechanical performance. By injecting supercritical CO2 in the mechanical recycling process, it is possible to eliminate volatile organic compounds (VOC), which are reduced by more than half compared to the conventional vacuum degassing process. The result is a recycled plastic pellet that is free of unpleasant odours. New LDPE films extruded from this recycled material have good processability without instabilities or gels . These films are not completely transparent, but have a translucent appearance with good optical properties in terms of gloss. Based on their mechanical performance, they can be reused in packaging and lightweight packaging applications.

Figure 3. LDPE pellet obtained in the sc-CO_2 extrusion process.

Figure 4. Blown film extrusion from LDPE pellets.

Figure 5. Extruded opaque sheet of thermoplastic material from printed film waste (left) and translucent sheet of granules obtained with the sc-CO_2 extrusion process.

Figure 6. Example of the application of shrink films in transport.

The two success stories mentioned above are fully aligned with the objectives of the circular economy. The promising results are leading to improvements in mechanical recycling processes to obtain high-quality plastic pellets that can be used to manufacture new products with greater added value. This helps close the life cycle of products so their value is maintained as long as possible and waste generation is reduced to a minimum.

AIMPLAS, the Plastics Technology Centre, provides services to help companies apply circular economy criteria to their business models and turn the legislative changes that affect the plastics industry into opportunities to improve company efficiency, reduce environmental impact and increase profitability. For this purpose, it works in research areas and projects that involve searching for applications to recover waste, improving the efficiency of recycling and upcycling processes, providing advice on the use of recycled plastics, and the characterization of plastic properties based on applicable regulations and use.