

Closing the Recycling Loop

Up-Cycling of End-of-Life Fluoroplastics

End-of-life fluoropolymers for different applications up to now required incineration. From today they can be decomposed into their monomers with a special method through chemical recycling. The new field of technology in this process is that virgin material is generated rather than recyclates.

It's almost impossible to imagine life without fluoropolymers, the high performance polymers used in sophisticated, everyday applications. They are essential to industrial applications and as part of a variety of consumer goods. Their manufacture requires significant amounts of energy and of raw materials, which is reflected in high material prices. An established recycling industry ensures that waste is collected throughout the value chain and, after reprocessing, is made available for a variety of other applications.

But what happens to fluoropolymer products when they have reached the end of their life cycle? To answer this question Dyneon GmbH in Burgkirchen, Germany, a 3M Company, has collaborated with the University of Bayreuth and In-VerTec, Osburg, Germany, on a project sponsored by the environmental foundation, Deutsche Bundesstiftung Umwelt. The aim of the project is to develop a method for recycling these end-of-life products into new products, with a high conversion rate and no loss of quality.

Existing Recycling Methods

Polytetrafluoroethylene (PTFE) is not processed using traditional thermoplastic methods such as injection molding or extrusion, but predominantly using a complex pressure sintering method followed by a machining process to produce the final part geometry. Owing to the large amounts of waste generated during production, and also as a result of the relatively high polymer price, a recycling industry sprang up in this sector at an early stage. Specialized companies recycle ma-



The Up-Cycling plant will initially process clean fluoropolymer materials, i.e., wet waste, off-specification materials of unfilled PTFE from manufacturers, and unfilled PTFE scrap

chining waste and off-cuts from PTFE processing using one of two different methods. In the first, remnants are cleaned, ground and then fed back into the product cycle as pre-sintered reprocessed PTFE for processing using ram extrusion, a special pressure sintering method. Alternatively, after preparatory steps such as sorting, cleaning and grinding, the PTFE polymer is degraded to approximately 1% of the original degree of polymerisation by using electron beams, gamma rays or thermo-mechanical degradation.

There is also a recycling strategy for waste such as sprues, typically produced in the injection molding of PFA (Perfluoroalkoxy alkanes) or FEP (Fluorinated ethylene propylene), the two completely fluorinated members of the fluorothermoplastic product group. Waste materials are ground, cleaned and then, following

granulation, fed back to be processed via injection molding or extrusion. This waste processing, however, is not the main focal point of the new 3M Up-Cycling concept, as there are already reprocessing and recycling systems in place. There are also existing markets for these recycled materials.

Previously, however, there were no opportunities to recycle products manufactured from PTFE, PFA or FEP when they reached the end of their life cycle. Such products include, for example, PTFE pipe liners in chemical plants, as well as other plant components like pumps, tank liners, seals, hoses, compensators and many other fluoroplastic components and systems.

The new Dyneon Up-Cycling method enables components to be recycled that were previously unable to be recycled. So, how does it work?

Process for New Materials

In contrast to existing recycling methods for fluoropolymers, this innovative process generates new materials rather than recycled materials. In the fluoropolymer sector, these new materials, which have not undergone any processing, are also referred to as 'virgin' PTFE, PFA or FEP. To bring the new Up-Cycling approach into operation, Dyneon collaborated with several institutions: Deutsche Bundesstiftung Umwelt (Federal Ministry for the Environment, Nature Conservation and Nuclear Safety), the University of Bayreuth and InVerTec, an institution for innovative process engineering. The laboratory phase of this process development has already been finished. A pilot plant with an annual capacity of 500 t of perfluorinated polymers (PFP) is currently being built and is expected to start operation in the second half of 2014 (Fig. 1). The intention is to increase the operational intake to full capacity by 2015.

The new high-temperature recycling process includes a grinding stage, after which the PFPs, which are preferably end-of-life products, are decomposed into their monomers at temperatures above 600°C. These monomers are the same chemical components from which the polymers were produced. This process called 'pyrolysis', primarily produces tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) with a recovery rate of 90–95%. The resulting



Fig. 1. Pilot plant of Dyneon for Up-Cycling of end-of-life fluoropolymers with an annual capacity of 500 t (figures: Dyneon)

gas mixture is then passed to the Dyneon monomer plant and cleaned by distillation. After this step, TFE with a purity of 99.9999% is obtained and can be used to manufacture arbitrary new fluoropolymers with no loss in performance. So the derived prod-

ucts differ in no way from the the source materials, whether it is a PTFE-product, a fluoropolymer or an elastomer. As a result, the description recycling is not considered suitable for this method, so it is now called Up-Cycling, and with good reason; products reaching the end of their life cycle are converted into new high tech products (Fig. 2).

Producing TFE/HFP monomers requires vast quantities of energy. The process needs more than 10,000 kWh/t, combined with a massive output of CO₂ during electricity generation. Other raw materials like fluorspar, CaF₂, chlorine and sulphuric acid are needed, while on the waste side, gypsum and hydrochloric acid are produced. Using the high-temperature pyrolysis method to produce monomers from used PFP products has a massive potential to save resources and to protect the environment at the same time (Fig. 3).

Cooperation with Partners for the Overall Concept

Previously, end products were predominantly disposed of in landfill or by incineration, with considerable associated »

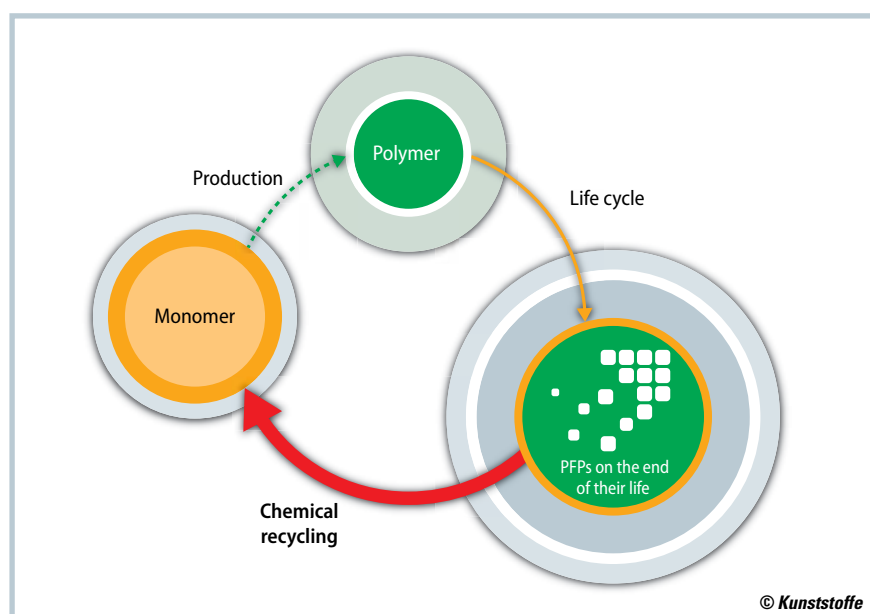


Fig. 2. Closing the life cycle loop: on reaching the end of their life cycle, components made from perfluorinated polymers (PFPs) are broken down into their monomers and fed back into the polymerization process

costs. Now they need to be collected, if possible at source at the end of their life cycle, pre-processed if necessary, and then transported back to raw materials supplier Dyneon. The structure and organisation of the logistic system is the responsibility of the company and its partners. However, products must be physically collected at source, by the operators of chemical plants, for example. This requires a comprehensive exchange of information to clarify a number of questions:

- Which products are suitable?
- Is product separation necessary?
- Do the products need to be pre-treated?
- How is the collection recorded for auditing purposes?

These are just a few questions that have to be clarified by intensive communication between the partners of the Up-Cycling process.

Often, PFPs are not in pure component form, such as PFA tubing or a PTFE pipe, but in the form of composites. In the context of chemical plant construction, this includes PTFE-lined pipes, tanks, pumps or distillation columns, in particular. Previously, it was only possible to dispose of these problematic parts via landfill, either as a composite, in individual parts or in fractions after a treatment process. Now, after a specialist company has separated steel and PTFE (PFP), there is the option of feeding all components back into the material cycle. As well as components from chemical plants, the new concept also focuses on recycling cables sheathed in fluoropolymers.

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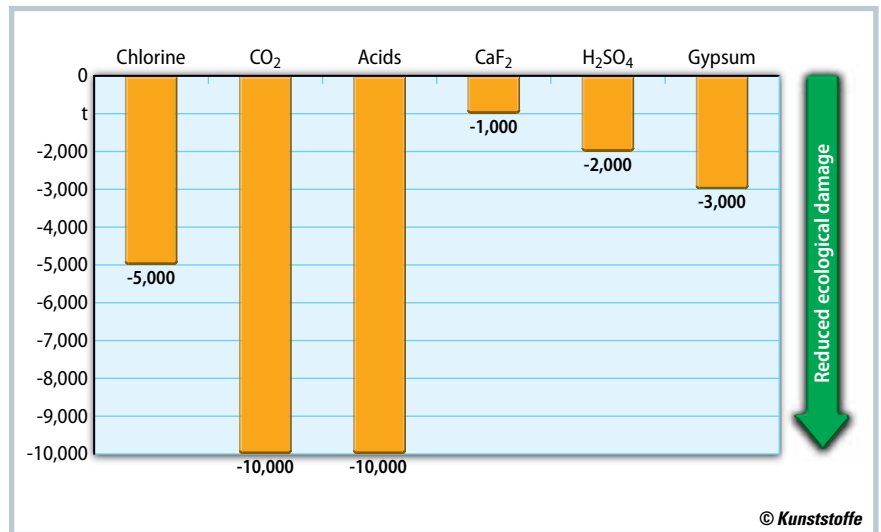


Fig. 3. Reduced environmental impact resulting from the new Dyneon high-temperature pyrolysis process; illustration shows the up-cycling of 1,000 t of PFPs

Product type	Material	Note
End-of-life components e.g. tube and pump linings, cable isolations	PTFE, modified PTFE, PFA, FEP	Separation from e.g. metal might be required
Processing wastes	PTFE, PFA and FEP compounds	Correct sorting is a precondition, filler has to qualified for Up-Cycling

Table 1. Perfluorinated polymer waste materials suitable for Up-Cycling

New Possibilities for Processing Companies

Although production waste from PTFE, PFA and FEP processing is currently successfully recycled by established companies using tried-and-tested methods, there are problems in this area for which there have been no worthwhile or technically feasible solutions to date. This includes PTFE compounds where basic PFPs contain fillers. Typical fillers include glass fibers, glass beads, coal, graphite and soot. Even in cases where recycling was technically possible, implementation generally failed as, owing to a lack of acceptance among end consumers, there was no opportunity to feed these recycled materials, with known disadvantages, back into the market (**Table 1**).

The global consumption of PFP raw materials in this problem category is currently around 25,000t per year. Whereas the pressure sintering process for PTFE compounds appears to be waste-intensive, with a waste rate of up to 75% not uncommon, fluorothermoplastic compounds can be processed with a much

lower proportion of waste. Taken together, the annual PFP compound waste disposed of in landfill is estimated at approximately 10,000–12,000 t. A tremendous potential to save landfill is, of course, a key part of the Dyneon Up-Cycling concept. Various correctly sorted compounds of processed waste have already been investigated for their suitability for Up-Cycling in the University of Bayreuth's laboratories.

Conclusion

The new Up-Cycling process offers the possibility to completely close the material cycle for PFPs and PFP-compounds. For the first time, components at the end of their life cycle and problem waste materials can be fed back into the value chain with a high conversion rate in the form of monomers. There is no loss in quality in the fluoropolymer products newly created by this process.

Collecting the recyclables, pre-processing them and Up-Cycling them to produce new primary products requires close cooperation between all the business partners involved. ■