Industrieverband
Halbzeuge und Konsumprodukte
aus Kunststoff e.V.

pro-K Fluoropolymergroup

Technical brochure 10

Recycling of Fluoropolymers

Preamble

The fully fluorinated polymer PTFE is the most widely used fluoropolymer and based on its unique properties established as an undispensible construction material in modern industries.

The main extraordinary properties of PTFE are resistance to most chemicals, a broad service temperature range, the excellent electrical properties, resistance to embrittlement, ageing resistance and very high purity.

Whereas for pure PTFE established recycling processes exist, many processors of PTFE compounds have to dispose their processing waste at high costs, mostly via waste dumps.
For pure fully fluorinated fluorothermoplastics there are also efficient recycling processes established. However pigmented or electrically conductive fluorothermoplastics must also be disposed at high costs.

Starting with fully fluorinated polymers a method has been implemented for chemical recycling in industrial scale.

This brochure informs about the different possibilities and processes to recycle fluoropolymers.

Important note:

This brochure is only for information purposes. The informations herein have been collected according in all conscience. The authors and pro-K don't accept any warranty for the exactness and completeness of the given informations. Each user has to make sure that the information is applicable and suitable for his purposes.

Status: May, 2018

Fluoropolymergroup
The Fluoropolymergroup is a product group of "pro-K Industrieverband Halbzeuge und Konsumprodukte aus Kunststoff e.V", Städelstraße 10, D-60596 Frankfurt am Main; Tel.: 069 - 2 71 05-31; Fax 069 - 23 98 37;
E-Mail: info@pro-kunststoff.de; www.pro-kunststoff.de

Content

1. Introduction

Based on its unique properties Polytetrafluoroethylene (PTFE) is established for many years as an indispensable construction material in modern industry. Due to its outstanding properties it is mainly used in very challenging applications. With a share of more than 50 %, PTFE is the most important representative of the fluoropolymers. Therefore the following information mainly refer to these grades.

PTFE is characterized by:

- Outstanding, nearly universal chemical resistance
- Broadest service temperature range
- Excellent dielectric properties
- Excellent non-stick and sliding properties
- No embrittlement or ageing

The properties of PTFE derive from its specific linear helical molecular configuration where the Fluorine atoms hermetically shield the carbon backbone. Due to the high carbon-fluorine bonding strength in combination with the high molecular weight of 10^7 – 10^8 g/mol, an exceptional thermal stability and a long service lifetime compared to other polymers are achieved.

According to different manufacturing processes PTFE is classified in

- Emulsion PTFE (E-PTFE)
- Suspension PTFE (S-PTFE)
- PTFE-Compounds
- PTFE-Micropowder

Most suspension PTFE grades do not contain any additives like emulsifiers that could lead to undesired emissions.

For the manufacturing of emulsion PTFE as well as for fluorothermoplastics, a fluorinated emulsifier is used which is highly recovered. The manufacturers of fluoropolymers organized in the Association of Plastics Manufacturers Europe (APME) have committed to abandon any perfluorooctanoic acid or their salts (PFOA resp. APFO) as emulsifier. Since 2015 this requirement is mandatory according to the European chemical legislation (REACh).

It is the responsibility of the manufacturer or distributor to assure that his products have been made without using PFOA or APFO.

PTFE-Compounds consist mostly of S-PTFE and inorganic or organic fillers. A separation of the single components is not possible - neither in the compound powder nor in the processed finished product.

PTFE micropowders are low molecular PTFE substances, which can be used as additive in different applications.

2. Legal requirements

European waste directive

The Directive 2008/98 EG on waste and repealing certain Directives lays down measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use. The five step waste hierarchy defines the priority order in waste prevention and management legislation and policy:

a) avoidance,
b) preparation for the re-use,
c) recycling,
d) other recovery (e.g. energy recovery) and
e) disposal.

The following stages describe the German way of waste regulation.
According to the “Kreislaufwirtschafts-/abfallgesetz (KrWG)” (= closed substance cycle waste management) waste disposal is only allowed if material or thermal recycling is not possible, due to technical, economical or ecological reasons.

According to §§ 6 – 8 KrWG dating from 2012 five stages in waste-management have to be observed:

Stage 1: Prevention of waste

Qualitative and quantitative prevention of waste, repeated use or longevity applications.
Examples:

- Increased use of isostatic moulding processes. Chipping waste is minimized when a pre-shaped form, close to the final dimensions is used.
- Based on the durability e.g. of pumps and containers which are made of fluoroplastics can be re-used in a further application. (Please note: Export restrictions must be considered.)

Stage 2: Preparation for re-use

Collect sorted disposal, avoid contamination, clean for re-use.
Examples:

- Grouping of processing machines and exhaust systems according to fluoropolymer categories
- Machining without use of lubricant and cooling liquids to prevent contamination

Stage 3: Material recycling

Collection of products with similar material properties, cleaning and processing, conversion into reprocessed PTFE resp. PTFE micropowder and Up-Cycling.

Up-Cycling is a thermo-chemical recycling, which splits the polymer back into the corresponding monomers, which, when cleaned, can be re-used for polymerization of nead fluoroplastics.

Examples:

- Collection of PTFE-waste, separated into standard and modified PTFE. Processing for the use as pre-sintered pellets for ram extrusion or, after radiation-induced degradation, for the manufacturing of PTFE micropowders.
- Fully fluorinated disposal of fluorothermoplastics is cleaned, pelletized and re-used either as pure regrind or blended regrind material for thermoplastic processing.
- Up-cycling (thermo-chemical) of end of life products made of PTFE, PFA or FEP

Stage 4: Other use

Other material recycling: PTFE and other fully fluoroinated fluoropolymers may not be used as substitute fuel for thermal incineration if its caloric value is below 11.000 kJ/kg (required according to §8 KrWG).
Examples:

- For sintered fluoropolymer waste there is a possibility to use it as flux in the cement or steel industry.
- For unsintered lathe chips there is a possibility of re-use as moulding powder provided that the waste can be milled to powder and the products are free of lubricants or cooling liquids.

Stage 5: Waste disposal

Incineration with insufficient energy use. Disposal of low-reaction materials.
Examples:
At present waste from PTFE-compounds can only be disposed at high costs.

To promote the re-utilization § 9 KrWG additionally requires to collect specific waste (like metals polymers etc.) separately.
If fluoropolymer waste is contaminated, they might fall in the class of dangerous substances. In this case there it is obligatory according to §50 KrWG to provide supporting documents about the disposal chain: „The producer, owner, collector, carrier and disposal companies have to prove the correct disposal of dangerous waste to the responsible authorities as well as among each other."
For this purpose the respective AVV-code has to be assigned.
Examples:

070213:	Plastic waste
120105:	Plastics and chips
200138:	Plastics
170204:	Plastics that contain dangerous substances

Depositing is only allowed if the waste in question does not emit dangerous substances, e.g organic components or soluble heavy metals and its caloric value is less than 6.000 kJ/kg. This is mainly the case with PTFE waste as its caloric value amounts to approximately 5.500 kJ/kg. If the caloric value exceeds 6.000 kJ/kg incineration of this waste is required. In this case it has to be ensured that the incineration plant chosen is equipped with an acid scrubber and the combustion temperature is above 800 °C. Metal pieces that contain PTFE and do not emit leachable components may be disposed in underground storage or in landfills belonging to class II (DepV Anh. 3. Furthermore it is possible to remove PTFE inliners mechanically and use them as feedstock for Up-Cycling. The remaining metal parts may be used as scrap metals in blast furnaces.

Waste from the manufacture and processing of S- and E- PTFE is usually sorted and can easily be recycled. The re-processing is performed by specialized companies. Typical products are micropowder and regenerated material for ram extrusion.

At the end of their life-cycle PTFE products are often contaminated with various other substances. In these cases a separate pre-treatment is necessary to prepare them for recycling.

As PTFE-compounds contain fillers recycling following present techniques is limited.

3. Recovery of PTFE and Fluorothermoplastics

There are several ways of the material recovery of fully fluorinated fluorothermoplastics:

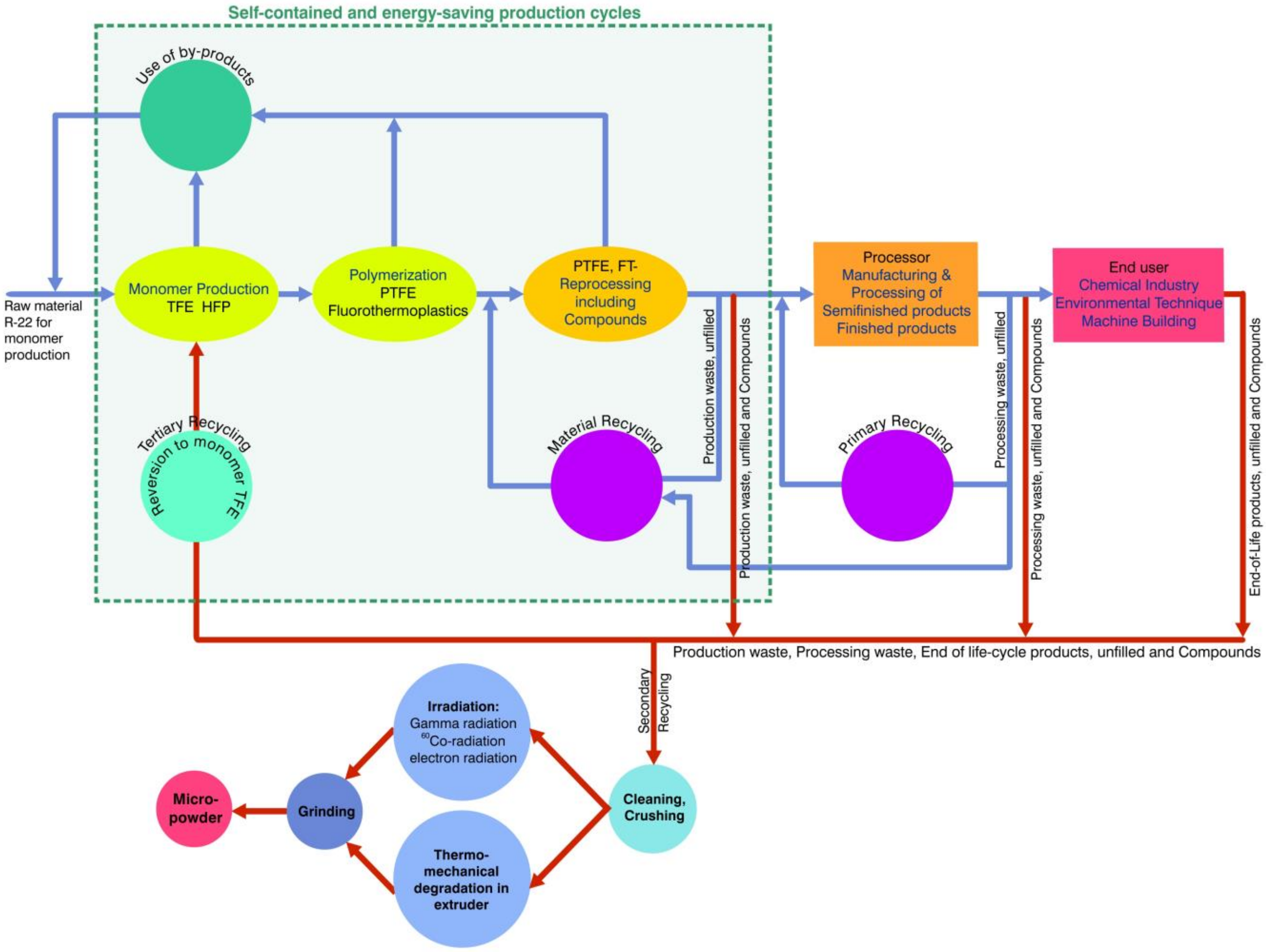

Fig. 1 Recovery cycle of PTFE and Fluorothermoplastics

3.1 Primary recycling

For primary recycling sintered PTFE waste is collected, sorted and ground to free-flowing powder. Reprocessing of pre-sintered PTFE is only possible if temperature and pressure are simultaneously applied e.g. in ram extrusion. The physical properties (e.g. tensile strength and elongation as well as cold flow) of regenerated PTFE differ fundamentally from those of virgin PTFE. (The differences can be seen in TB-04.) Addresses of appropriate recycling companies are listed in the attachment.

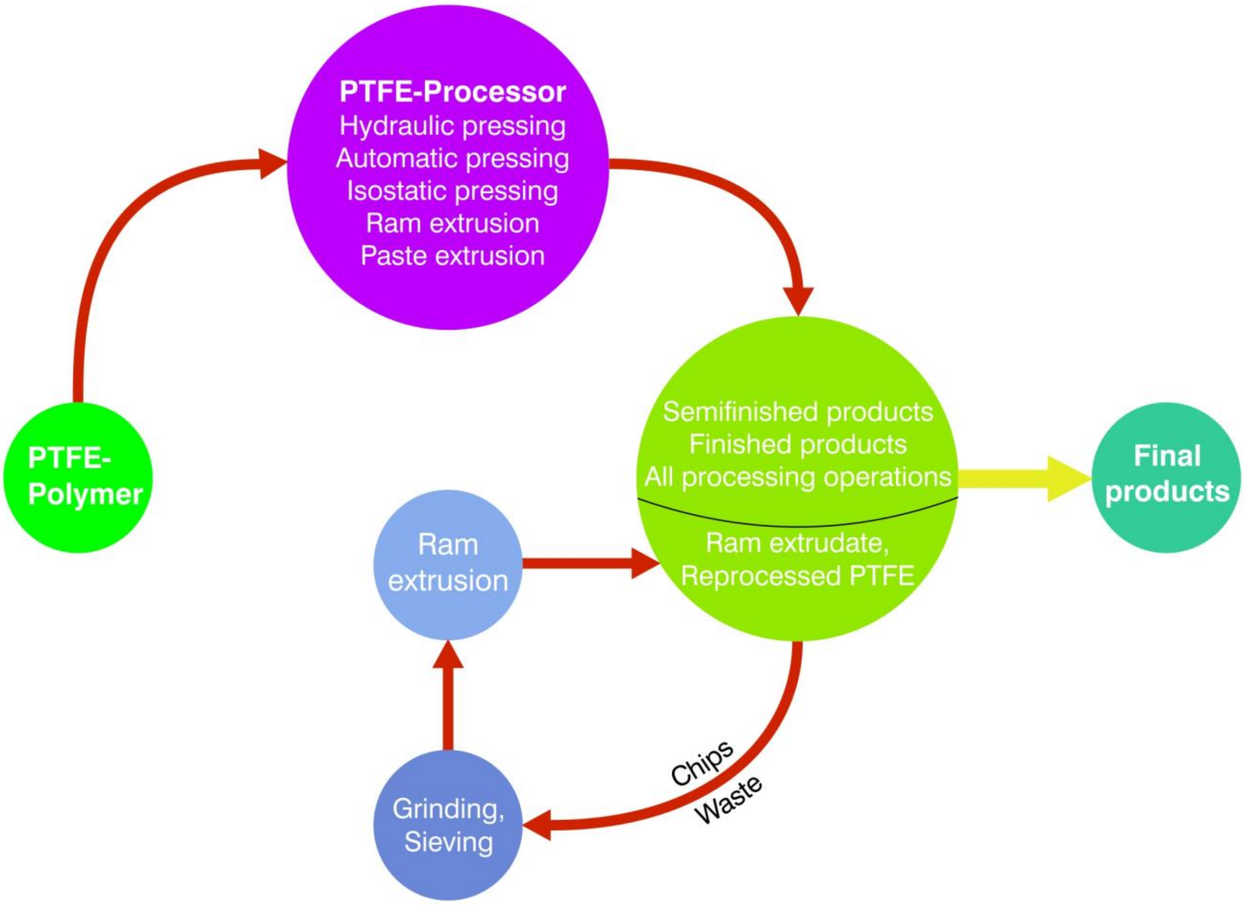

Fig.2 Primary recovery circuit

3.2 Secondary recycling

In contrast to primary recycling secondary recycling is characterized by the degradation of high molecular PTFE to PTFE-micropowder. This can be achieved either by thermo-mechanical degradation or by degradation using irradiation with high energy radiation. Typically, radiation sources implemented in medical technology are used:

- Gamma-radiation of a ^{60}Co-source
- Beta-radiation: E-Beam

The irradiation process is supplemented by a grinding step in order to achieve the desired particle size. Owing to this process, which strongly reduces the molecular chain to around 1% of their original chain length, the properties of the degraded PTFE change remarkably. Therefore the products obtained from this process cannot be used for typical PTFE applications. However the PTFE micropowders manufactured according to the described processes are suitable as additives for manifold applications. Additives of this kind can be found in:

- Non-PTFE plastics to improve the gliding properties
- Non-PTFE plastics to improve the processing properties
- Lubricants to improve the lubrication properties
- Elastomers to improve the non- stick properties
- Printing inks to reduce the stickiness/soiling of the surface
- Coatings and paints to improve the processing and non-stick properties

Irradiation as a process is technically so advanced that also additives for plastics that may come into repeated contact with food can be produced in this way (FDA approval).

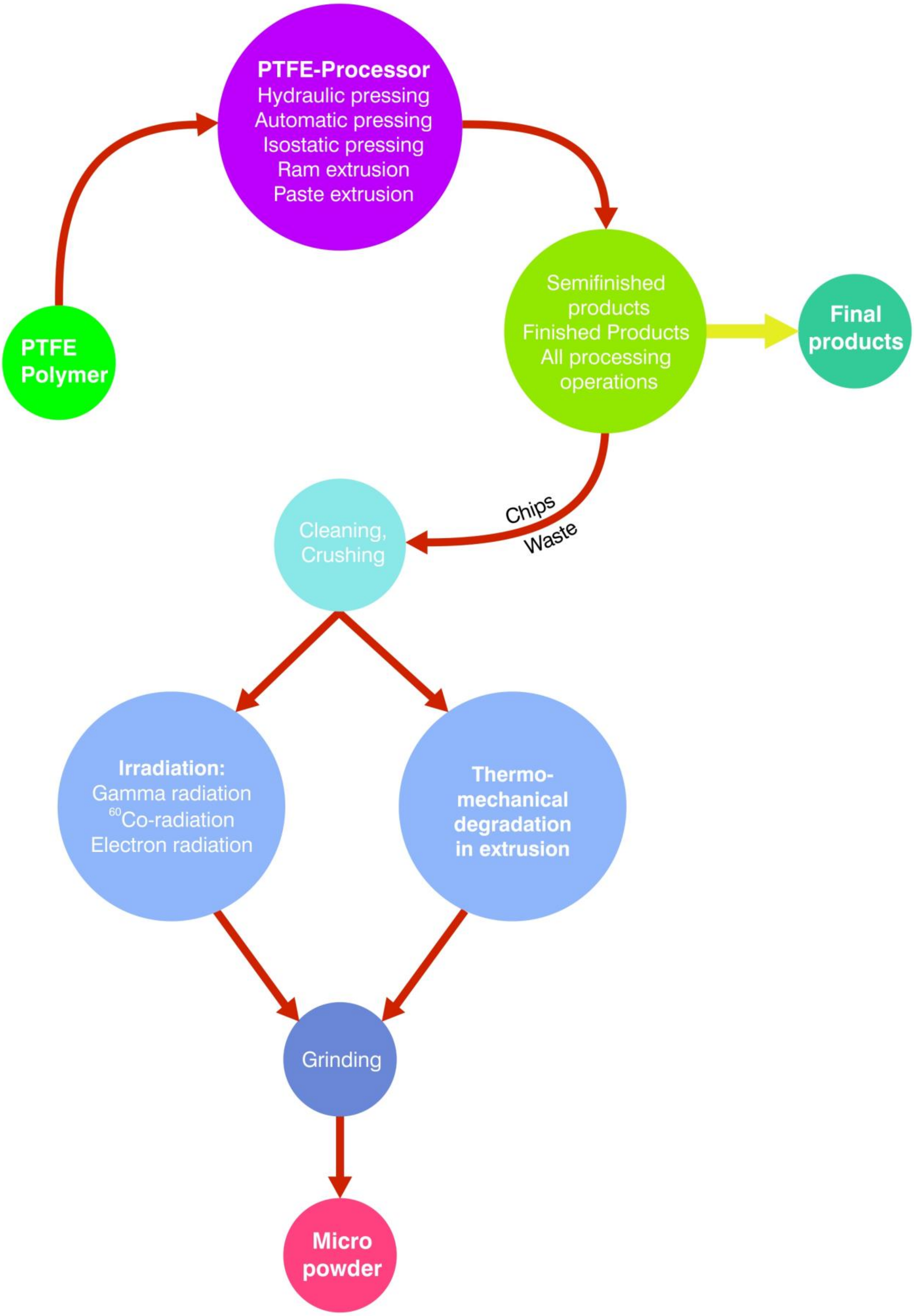

Fig.3 Secondary recovery circuit

3.3 Tertiary recycling = so called Up-Cycling

This process consists of the pyrolysis of PTFE under inert atmosphere. It yields monomers like Tetrafluoroethene (TFE) and Hexafluoropropene (HFP) in large quantities.
The advantage of this process is that not only homogenous PTFE but also fully fluorinated fluorothermoplastics like PFA or FEP can be utilized. Even compounds, especially those with mineral fillers, can be recycled that way

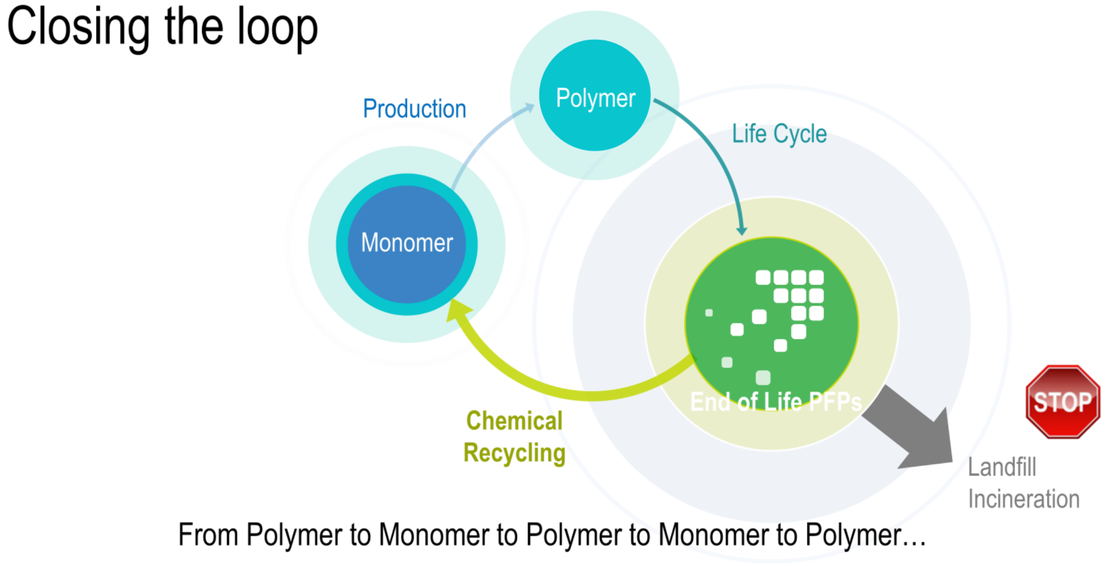

Fig.4 Up-cycling circuit

Since this recycling process can only be operated within an existing infrastructure for the recovery of fluoromonomers only companies which are correspondingly equipped are qualified.

4. Recycling of Fluorothermoplastics

According to the EU-Legislation fluorothermoplastics should be recovered thermally if mechanical recycling is not possible.
For fluorothermoplastics several variations of the primary recycling are state of the art. During film extrusion trimming waste is directly pelletized and re-fed to the film extruder. Start up- and shut-down material, that may differ in their properties from the finished product, are collected as mono fraction, cleaned pelletized and directly used in the thermoplastic processing. This means that they may not be suitable for all applications. In the meantime these products have already found a sound place in the market. Examples are tubes and clamping systems in the architecture and power plant construction.
If for technical or other reasons a primary recycling for fluorothermoplastics like PFA or FEP is not possible they may be used in the tertiary recycling or Up-Cycling.

Industrieverband
Halbzeuge und Konsumprodukte
aus Kunststoff e.V.

5. REACh

As all other polymers also fluoropolymers are exempted from REACh Regulation. This includes PTFE Micropowders and Fluoropolymer recycled materials.
Nevertheless each supplier of fluoropolymers, whether of new or recycled materials has to provide a Safety Data Sheet.

6. Storage and transport packaging

After implementation of the German Packaging Ordinance, also known as „Verpackungsverordnung“ in 1991, distributors or producers are obliged to take back empty packaging and re-use them.

7. Attachment

7.1 Companies which perform recycling of PTFE-products:

7.1.1 Fluorothermoplastics, FTP:

- **Aturon GmbH**, Parkweg 3, CH 9443 Widnau, Tel.: +41 (0)71 351 47 61, www.aturon.ch
- **Heroflon S.p.A.**,Via de Gasperi 4, I 25060 Collebeato, Italien, Tel: +39 030 2510211, www-heroflon.com
- **MINGER Kunststofftechnik AG**, Industriestrasse 19, CH-9050 Appenzell, Tel.: +41 71 788 01 20, www.minger.ch
- **Trifluor Kunststoff GmbH**, Am Langenhorster Bahnhof 18, 48607 Ochtrup, Tel: +49(0)2553 93640, www.trifluor.de

7.1.2 Polytetrafluoroethylene, PTFE:

- **Heroflon S.p.A.**,Via de Gasperi 4, I 25060 Collebeato, Italien, Tel: +39 030 2510211, www-heroflon.com
- **Shamrock Technologies BVBA**, Heersterveldeweg 21, B-3700 Tongeren, Belgien, Tel.: +32 (0)12 45 83 30, www.shamrocktechnologies.com
- **Mikro-Technik GmbH & Co.KG**, Industriestrasse 4, D-63927 Bürgstadt, Tel.: +49 (0)9371 4005-43, Fax.: +45 (0)9371 4005-70, www.mikro-technik.com **MINGER Kunststofftechnik AG**, Industriestrasse 19, CH-9050 Appenzell, Tel.: +41 71 788 01 20, www.minger.ch
- **United Polymer Mixers**, Ramgatseweg 14, NL-4941 VS Raamsdonksveer, Niederlande, Tel.:+31 (0)1625 14 945, www.upmkunststoffen.nl

7.2 Companies which operate Up-Cycling of PTFE and selected PTFE-compounds as well as fully fluorinated Fluorothermoplastics,

- Dyneon GmbH, Bau 172, Industrieparkstrasse 1, D-84508 Burgkirchen, www.3M.com; Marc Lenczyk, Tel.: +49 8679 76417

7.3 Caloric values of fluoropolymers

- PTFE 5400kJ/kg
- PTFE Glascompounds 5020kJ/kg

8. Glossary

Waste balance

The waste balance collects the character, amount and final disposition of waste that incurs during a defined time frame in a specific area. Waste balances may be established e.g. for single companies, parishes or federal states. The German closed substance cycle waste management (KrWG) requires that waste generators have to establish a waste balance if they produce a certain amount of requiring supervision waste or waste according to the AVV-code per year.

Regulation of waste register (Regulation of the European waste register)

The waste register regulation defines the labeling of waste as well as their classification according to their hazard class. For the identification the appendix of the regulation (Abfallverzeichnis) contains waste types and six figure codes. The AVV transforms the European waste register into German legislation.

Waste hierarchy

An essential part of the closed substance cycle waste management (KrWG) is the five stage waste hierarchy, which is regulated in §6. The default was fixed in the European waste framework directive. It defines a waste sequence hierarchy according to:

1. Avoidance
2. Preparation for the re-use
3. Recycling
4. Other utilization, especially energetic utilization and backfilling
5. Disposal

Despite this obviously strict sequence the protection of human health and environmental protection have to be treated in first priority. Do not neglect technical-, economical- and social aspects.

A discussion is ongoing about the definition between the steps 2, 3, and 4. In individual cases it is not always clear which option is the best. Since the best option is not defined for each type of waste the so called heat value criteria is a transition regulation. This means that the energetic utilization of waste with a heat caloric value of >11.000 kJ/kg is from an ecological point of view equivalent to a mechanical utilization and is therefore accepted. This clause caused many discussions in the past in the forum of waste industry processors. Due to this uncertainty the German Federal Government announced during mid of 2016 to change this clause. Only in exceptional cases the energetic utilization shall be preferred above the mechanical utilization.

Cradle to Cradle

Cradle to cradle is a design concept for manufacturing. Products are designed in a way they can be composted or up-cycled into their components at end of life. Waste does not occur in the cradle to cradle concept - everything is introduced again in the economic cycle.

Energetic recovery

If material recycling of waste is not possible, energetic recovery is an option. The energy out of burned waste is used to produce heat or electricity. Waste is used as surrogate fuel (EBS) or in garbage incineration plants. In the EU Legislation material recycling is preferred.

Energy efficiency

Energy efficiency is the amount of energy that must be spent to gain a defined benefit: e.g. to cool grocery in a refrigerator. The less energy is necessary to achieve this benefit the more efficient is a process or a device. Since 1998 the European Union classifies the energy efficiency of household appliances by the energy label 7/34.

European waste directive

The Directive 2008/98 EG on waste and repealing certain Directives lays down measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use. The five step waste hierarchy defines the priority order in waste prevention and management legislation and policy:

a) avoidance,
b) preparation for the re-use,
c) recycling,
d) other recovery (e.g. energy recovery) and
e) disposal.

Hazardous goods

Substances, formulations (mixtures, batches, solutions) or articles are called hazardous goods if they contain components which cause danger for the public safety because of their physical or chemical properties. This is especially true for the community, important common property, life and health of humans, animals and others. These goods must be classified as hazardous goods.

Gross calorific value / Net calorific value

The gross calorific value is the maximum heat out of combustibles bringing all combustion products back to the original pre-combustion temperature, and in particular condensing any vapor produced. Subtracting the heat of vaporization of the water leads to the lower heating value (net calorific value). These values are related to the mass and indicated in kJ/kg. By definition the net calorific value is used for technical applications as heating value for fuel or waste. As in most plants the water vapor exhausts and cannot be used for the generation of energy. As the detection of the net calorific value is often difficult in most cases the gross calorific value is investigated. It defines the amount of heat without consideration of condensation and is therefore in most cases higher than the net calorific value. In the following the condensation enthalpy is subtracted from the calorific value. In most cases the net calorific value is 10% below the gross calorific value. In the waste economy the heat value criteria is mostly used when burning waste.

Sustainability

Sustainability in general means the equitable consideration of ecological, social and economic aspects. Sustainable actions ensure the welfare of environment, society and economy also in the future.

Eco-balance

The eco-balance is an instrument which shows the environmental influences and the resulting ecological damage of a product all over its life cycle. The eco-balance is a guide to decide on ecological improvements within a product life cycle. It is important for the selection and use of packaging materials.

Product stewardship

The product stewardship was first introduced in Germany in 1991 by the packaging ordinance for a sub domain of the waste legislation. It describes the responsibility of a manufacturer or distributor for the complete life cycle of a product, from manufacturing to disposal. Main target is the comprehensive liabilities for retraction, recovery and returnables. According to the regulation on packaging, each enterprise that puts packaging into the market has to retract it after use and deliver it to recovery. By the EU Legislation the product responsibility was defined as prerequisite for constructive circular flow economy and extended to all consumer goods and commodities.

REACh Directive for the Registration, Evaluation, Authorization and restriction of Chemical substances

The directive for the registration, evaluation, authorization and restriction of chemical substances is the legislation of chemicals of the European community. The directive has been effective since June 2007. For the registration there are different transition periods depending on the substance and their amount. 2018 latest also chemicals used in small amounts (>1 to per year) have to be registered at the agency for chemical substances – ECHA in Helsinki. Waste and polymers are exempted from the registration. The target of REACh is to protect human health and environment from possible chemical related risks.

Recycling

Recycling is the re-introduction of used materials (among others: packaging) into the cycle of materials. Materials are collected, sorted and refined to be re-used as material or energy source. Recycling can help to preserve resources and avoid waste.

Direct reduction method

The direct reduction method is a technique used for the iron manufacturing. Plastic pellets are added to iron ore in a blast furnace. At 2000°C its carbon detracts the oxygen from the ore, producing raw iron. The plastic waste replaces heavy crude oil.

Regrind

Thermoplastic polymers are normally offered as granules to the plastics processing industry. These lenticular or cylindrical polymer particles are free flowing and can be easily transported in bags. The material is called regrind if it is made from used plastics.

Recycled material

Recycled material is an umbrella term for plastics which are recovered from plastic waste. Regrind is part of that.

Feedstock recycling

The feedstock recycling degrades used plastics into raw materials like oil, methanol or carbon monoxide. These newly formed chemical resp. petrochemical precursors or raw materials are re-introduced in the cycle of materials. The most important processes of feedstock recycling are the direct reduction method and the methanol production.

Secondary feedstock

Raw materials gained from recycling and used as starting material for new products are called secondary feedstock. In municipal solid waste f.e. packaging material like glass, paper, plastics aluminum, tin plates and composites are re-introduced in the production process by different recovery techniques.

Material recovery

Material recovery means that secondary feedstock is used. In common language material recovery is also called recycling. It can be differentiated between material and raw material recovery.
The material recovery uses waste as feedstock for a new product, e.g. plastic granules. If waste is divided in its components and used as feedstock replacement we are talking about feedstock recovery.
A material recovery is, among others, possible with metals, plastics, glass and paper. For this the waste is mostly collected separately or afterwards classified in treatment plants. Depending upon the waste it is treated in a way that it can be used again as secondary feedstock in the production.
According to the five step waste hierarchy of DIRECTIVE 2008/98 the material recovery has to be preferred to the energetic recovery.

Up cycling

Up cycling is the process of transforming by-products, waste materials, useless, or unwanted products into new materials or products of better quality or for better environmental value. For the up-Cycling the waste needs not always be recycled extensively. Sometimes the waste is just converted. An example is a candleholder made out of a beer bottle.
The opposite of up cycling is down cycling. In this case it is not possible to treat the waste so that the resulting secondary feedstock has the same quality than the original primary feedstock

Recovery

Regulations about the recovery of waste are regulated in the DIRECTIVE 2008/98. Basically recovery is preferred. The recovery is differentiated in material or energetic recovery. According to the five step waste hierarchy the material recovery has priority to energetic recovery and in the next step disposal. At the end of the day the most environmentally safe option has to be chosen. The material recovery is differentiated in three categories:

- The substitution of primary raw materials by those generated out of waste, e.g. paper filaments from used paper, steel from scrap metal.
- The use of the material properties of waste for the original purpose like the conditioning and refinement of waste oil for the production of new oil.
- The use of material properties of waste for other purposes like compost from organic waste as soil improver