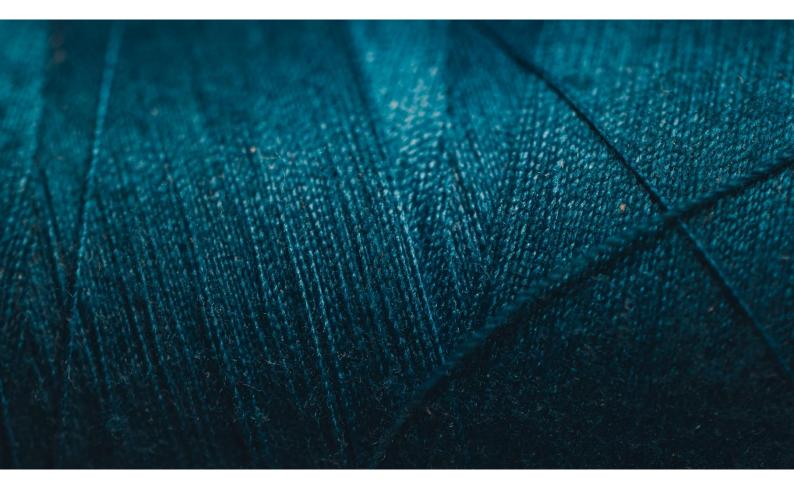


CHEMICAL RECYCLING OF TEXTILES

June 2024



To promote circularity and minimise the impact of the Textile and Footwear Sector, **recycling is the preferred option when reuse or repair are no longer possible.** New chemical recycling technologies have been developed in recent years. They complement mechanical and thermomechanical recycling technologies, which are more mature but have certain limitations (inability to separate material blends, or colours, reduction in the length of fibres after tearing, etc.). Recycling post-consumer CHF¹ waste remains a major challenge, as the waste is extremely heterogeneous and complex due to the presence of numerous materials (often in blends), hard points (buttons, fasteners, etc.) and contaminants (dyes, primers, additives) that can disrupt recycling efficiency.

¹ CHF: Clothing, Household linen and Footwear



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Sources

This Refashion summary is a continuation of the two webinars on chemical recycling presented by Refashion and Dr. Arnaud Parenty (Lavoisier Circular Transition), which you can watch again in <u>replay</u>. Refashion would like to thank Arnaud Parenty, engineer and doctor in organic chemistry, and member of the Refashion Scientific Committee, for his support on the subject of chemical recycling of textiles.

The data on the fractions of the various textile materials in the non-reusable waste stream leaving sorting centres are taken from the <u>characterisation study of the incoming and outgoing streams from</u> <u>sorting facilities</u> (Refashion, 2023) [1].

This note is also based on the following two scientific publications:

- Loo, S.-L., Yu, E., & Hu, X. (2023). Tackling critical challenges in textile circularity: A review on strategies for recycling cellulose and polyester from blended fabrics. *Journal of Environmental Chemical Engineering*, 11(5), 110482. <u>https://doi.org/10.1016/j.jece.2023.110482</u>
- Tonsi, G., Maesani, C., Alini, S., Marco, O., & Pirola, C. (2023). Nylon Recycling Processes: A Brief Overview. Chemical Engineering Transactions, 100, 727–732. <u>https://doi.org/10.3303/CET23100122</u>



Definitions & Processes

Textile fibers

Different fibres are used in the manufacture of textiles (clothing, household linen) and determine chemical recycling processes. A distinction is made between natural fibres and man-made fibres, either from natural resources (artificial fibres) or from petrochemicals (synthetic fibres). Textile fibres are essentially made up of polymers, i.e. an assembly of macromolecules called monomers joined together by bonds.

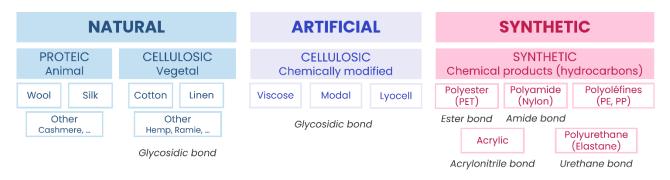


Figure 1: Classification of fibers used in textiles

Natural

Cotton, like other natural cellulose-based fibres (flax, hemp, etc.), has a complex chemical structure consisting of multilayered tubes. It is composed mainly of cellulose, but also includes hemicellulose and proteins.

This category also includes protein-based fibres such as wool and silk, which have amide bonds and can therefore also be compared to acrylic fibres.

Artificial

Artificial cellulosic fibres (viscose, modal, lyocell, etc.) are derived from cellulose.

Synthetic

In clothing textiles, the polyester used is polyethylene terephthalate (PES or PET), while polyamides (PA) are mainly aliphatic polyamides: PA 6-6 (nylon 6-6) and PA 6 (nylon 6).

The term "acrylic" fibre is a misnomer. These are polyacrylonitrile fibres, which include "acrylic" and "modacrylic" fibres. "Acrylic" fibres are composed mainly of acrylonitrile (>85%) and co-monomers (vinyl acetate, methyl acrylate), while "modacrylic" fibres are composed of acrylonitrile in lower proportions (35-85%) and different co-monomers (PVC, PVDC, vinyl bromide).



Chemical recycling processes

Chemical recycling is defined as "the conversion into monomers or the production of new raw materials by modifying the chemical structure of plastic waste [...] with the exception of energy recovery and incineration" (standard ISO 15270). In the case of textiles, chemical recycling consists of **breaking down textile waste into polymers and/or monomers** using chemical processes. **These outgoing products are then converted to new fibres for the textile industry (closed loop) or products for other sectors (open loop).**

Chemical recycling can be divided into two main technologies: dissolution and Depolymerization.

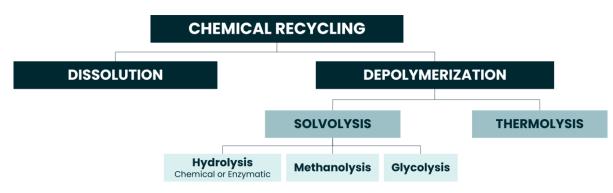


Figure 2: Classification of the main chemical recycling processes

Chemical dissolution

It consists of **selectively separating a material by dissolving chemical compounds in one or more specific solvents.** The **basic components** of the materials are then recovered after filtration, purification, and precipitation.

Developed for all fiber types

Characteristics:

• Allows partial purification of the polymer: the elimination of impurities will depend on their solubility in the solvent used. An impurity that is not soluble in the solvent will be easily eliminated, and vice versa.

It should be noted that chemical dissolution is not included in the normative definition of chemical recycling because it breaks down but generally does not modify the polymer's structure. Nevertheless, it is commonly considered to be a chemical recycling process.



Depolymerization

It consists **in breaking down the polymer chains to convert it into monomer(s) or polymer with a relatively lower molecular weight** (partial depolymerization).

More developed for synthetic fibers

Characteristics:

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- Requires extensive purification steps both upstream (input) and downstream (output).
- Allows almost total elimination of contaminants, additives, and other impurities, effectively converting it to virgin material (monomer) with its properties.

2 main depolymerization routes:

Solvolysis: chemical depolymerization

It relies on the use of a reactive **solvent capable of depolymerizing the polymer**. Catalysts are generally used to accelerate the reaction. There are also "enzymatic" depolymerization processes: the polymer is degraded under mild chemical conditions using a selective enzyme. Chemical or enzymatic solvolysis is used to **obtain monomers**. Depending on the solvent used for the reaction, various processes can be distinguished, with the main 3 being:

Hydrolysis Solvent : Water

The process can be carried out in acid, neutral or basic conditions. It can be relatively long, requiring high temperatures and pressures. Methanolysis Solvent : Methanol (alcohol)

The presence of water can disrupt the process. Separation and refining of the resulting products can be costly. Glycolysis Solvent : Ethylene glycol (alcohol)

The process is relatively flexible, simple and mature. It is the least energy-consuming of the 3 solvolysis processes.

Types of bonds to break: cellulosic, ester, amide, urethane

Thermolysis: thermal depolymerization

It involves **heating the polymer to very high temperatures in an inert atmosphere** (lack or absence of oxygen), using technologies such as **pyrolysis or cracking**. The result is a mixture of oil, gas (syngas) and solid compounds. These products are then converted into chemical raw materials.

Types of bonds to break: alkane

Thermolysis is therefore applicable to polyolefins, but polypropylene is a less common material mainly found in technical garments (sportswear). **It is not suitable for other textiles**, as it cannot depolymerize the main polymers (polyester, acrylic, polyamide), as high temperatures lead to the production of CO/CO2, charcoal, or polymer cross-linking.



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Chemical recycling of single-material textiles

Single-material textiles are made from one single type of material. Single-material textiles account for more than half of the post-consumer textile waste (55.8% by weight) analyzed in the 2023 Refashion characterization study [1].

Cotton and other cellulosic fibers

Cotton is the dominant material in non-reusable textiles leaving sorting centers [1]:

Composition Cotton in outgoing streams from sorting facilities

Rank: 1st Global share (pure/blend): 43% Share of 100% cotton: 27.6%

Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles. Composition Artificial Cellulosic Fibers in outgoing streams from sorting facilities

Global share (pure/blend): 6% - Rank: 5th Share of 100%: 1.4% - Rank: 12th

Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles.

Preferred chemical recycling routes? Chemical dissolution

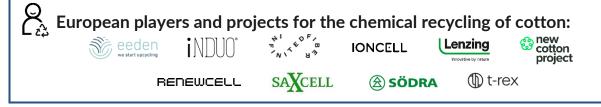
The aim is to **isolate the cellulose and recover it in the form of cellulose pulp**, which is then used to produce new cellulose artificial fibers. The dissolution process affects the structure of the cotton, making it **impossible to recover cotton fibers**. These processes achieve **TRLs of 7 to 9 (i.e. industrial) for pure textiles** (e.g. 100% cotton).

Challenges: choosing the right solvent to avoid the cellulose degradation and maintain a high concentration of it in the resulting product, limiting temperature rise, non-toxic.

There are two dissolving techniques:

- **Direct dissolution**: similar to traditional processes for manufacturing cellulosic manmade fibers (viscose, Cupro, Lyocell, Ioncell), this involves using chemical agents to dissolve the cellulose.
- **Dissolution by "derivatization"**: modification of cellulose into a derivative with a similar chemical structure to facilitate dissolution (xanthation, nitration, esterification, etherification). Note that this can modify the cellulose, hence it may not be possible to remake artificial fibers.

Other routes: depolymerization by solvolysis, more specifically **chemical or enzymatic hydrolysis**, depolymerizes cellulose to obtain its monomer: glucose (a platform molecule for plastics processing).





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Polyester Polyester is the 2nd most common material after cotton in non-reusable textile waste leaving sorting centres, according to the results of the 2023 Refashion characterisation study [1]: **Composition Polyester** in outgoing streams from sorting facilities Rank: 2nd Global share (pure/blend): 19% Share of 100% polyester: 11% Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles. (2)) (2) Preferred chemical recycling routes? **Depolymerization by Solvolysis** The aim is to return to monomers and then resynthesize polyester. These chemical or enzymatic polyester depolymerization technologies are currently in the process of industrialization (TRL 4 to 7). The 3 main technologies are : Hydrolysis: Obtains TPA and MEG (PET monomers). Methanolysis: Obtains DMT and MEG (PET monomers). Glycolysis: Obtains BHET (PET monomers). Other routes: dissolution is less studied for pure polyester, as polyester is difficult to dissolve in a solvent. European players and projects for the chemical recycling of polyester: DePoly EASTMAN ioniga Axens JEPLAN CARBIOS Energies nouveller

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POSEIDON PLASTICS

loop

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white cycle



Polyamide

Polyamide fibers are less present than cotton and polyester in non-reusable streams leaving sorting centers, according to the results of the 2023 Refashion characterization study [1]:

Composition Polyamide in outgoing streams from sorting facilities Global share (pure/blend): 4% - Rank: 7th Share of 100% polyamide: 1.3% - Rank: 13th

Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles.

Preferred chemical recycling routes?

Chemical recycling of polyamide is more complicated than that of polyester, as the amide bond is difficult to "break" and different polyamides (PA 6, PA 6-6) are used in the manufacture of clothing. These textiles are often "contaminated": mixed with other materials (wool, cotton), functionalized (anti-UV treatment, coating) or processed with dyes that are difficult to remove (acid dyes).

An initial technology for **depolymerizing PA6 (nylon 6) has just reached the industrial stage (TRL 9).** However, the majority of industrialized solutions for the chemical recycling of polyamide textiles are limited to fishing nets, carpets, post-industrial waste (PA 6) and airbags (PA 6-6). **Ongoing research aim** to further develop processes adapted to post-consumer clothing textiles:

- Depolymerization by solvolysis: the amide bond is difficult to "break" and requires processes at very high temperatures (melting point > 260°C), with the use of catalysts, basic or acidic solutions, etc. Hydrolysis with an acid solution is currently the most widely developed technique for depolymerizing PA6 (nylon 6). Given these constraints, enzymatic depolymerization could be a promising future pathway, yet further research is needed to optimize the process and ensure its economic viability.
- **Chemical dissolution**: this route, still under development, also **looks promising** for overcoming the constraints of depolymerization.

$\bigcup_{i=1}^{\infty}$ European players and projects for the chemical recycling of polyamides:

ECONYL TECHNYL 4EARTH (D t-rex

CEA, Upnyl-tex project, Innovation Challenge 2023.

Review: Amiridis et al., 2004. https://doi.org/10.1002/pen.10845

PolynSPIRE, Ljubana University, 2020. https://doi.org/10.1021/acssuschemeng.0c05706

Pham *et al.*, Innsbruck University, 2021 & 2023. <u>https://doi.org/10.1002/app.51170</u> <u>https://doi.org/10.1002/app.53813</u> Xueli, W. *et al.*, Donghua University, 2023 <u>https://doi.org/10.1177/00405175221148260</u>

Papaspyrides, C. D. *et al.*, Athens University, 2002. <u>https://doi.org/10.1002/app.11147</u>



Acrylic

Acrylic textiles account for a significant proportion of non-reusable streams leaving sorting centers, according to the results of the 2023 Refashion characterization study [1]:

Composition Acrylic in outgoing streams from sorting facilities Global share (pure/blend): **12%** - Rang : **3**rd

Share of 100% acrylic: 6.9% - Rang : 5th

Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles.

Preferred chemical recycling routes? Chemical dissolution

The presence of numerous monomers and components such as chlorine and bromine complicate the recycling of acrylic and modacrylic textiles by chemical means. Processes are still at the **development stage**.

Dissolution in organic solvents or aqueous solutions is the **most promising** chemical route.

Other routes: depolymerization by solvolysis does not break the carbon-carbon double bonds necessary for the return to the monomer form.

 \bigcirc \bigcirc \bigcirc Players and projects for the chemical recycling of acrylic:

🊺 regel"

REACT European Project, 2019-2022. https://cordis.europa.eu/project/id/820869



Chemical recycling of 2-material blends

The term bimaterial refers to textiles made from **two different types of fiber**. When one component predominates (>90%) in biomaterial blend, the same recycling processes are used for this majority fiber as for monomaterial textiles. Blends account for almost 45% of post-consumer waste, with a prevalence of two-material blends representing over a third of the textile waste (35%) analyzed in the 2023 Refashion characterization study [1].

Polyester/Cotton

Polyester/cotton blends, also known as "**polycotton**", are the **material blends most commonly used in textiles** and most often found in non-reusable streams leaving sorting centers [1].

Composition Polycotton in outgoing streams from sorting facilities Rank: 3rd Share of blend polyester/cotton : 8.8% Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles.

Preferred chemical recycling routes?

Multiple methodologies can be implemented, with the aim of **separating polyester fibers (PET) and cotton (cellulose)**, then filtering the resulting products to recover the components separately. The **main approaches** available today are:

Cellulose dissolution & Hold PET Outgoing products:

cellulose pulp + polyester

Cellulose degradation & Hold PET Outgoing products:

glucose + polyester

Hold cellulose & PET depolymerization Outgoing products: Cotton + PET monomers Successive dissolutions of cellulose and PET

Outgoing products: cellulose pulp + polyester

There are also academic projects and work on processes:

- of successive degradations
- of total and concomitant degradation of cellulose and PET.

Reminder: cotton loses its structure during dissolution. The cellulosic pulp obtained can be used to produce cellulosic man-made fibers.

 $\bigcup_{i=1}^{n}$ European players and projects for the chemical recycling of polycotton:





Blends with Polyamide(s)

Polyamides are **mostly blended** in textiles (~80% blended versus 20% pure polyamide), mainly with wool, elastane, cotton or viscose.

(L)

Preferred chemical recycling routes?

The recycling of 2-material blends containing polyamide is still at the academic stage. It is being carried out on "model" blends.

PA6-6/Wool 50/50 or PA6-6/Cotton 50/50

PA6-6 dissolution & Hold Wool/Cotton Solvent: CaCl2/Ethanol/Water Temp: ambient PA6/Polyester or PA6/Cotton or PA6/Polyurethane

PA6 dissolution & Hold other materials Solvent: CaCl2/Ethanol/Water Temp: 75°C

PA6/PA6-6

Dissolution of the 2 PAs and controlled precipitation

Selective dissolution of one PA (solvent or temperature)

Difficulties:

- Cotton's high solvent absorption necessitates significant solvent volumes
- Solvent extraction from the fiber, especially calcium chloride (CaCl2)
- Complexity in separating PA6 and PA6-6 due to their closely related chemical structures.

\bigcirc \bigcirc \bigcirc \bigcirc Research on the chemical recycling of polyamide blends:

-@collant

Pham *et al.*, Innsbruck University, 2021 & 2023. <u>https://doi.org/10.1002/app.51170</u> <u>https://doi.org/10.1002/app.53813</u> Xueli, W. *et al.*, Donghua University, 2023 <u>https://doi.org/10.1177/00405175221148260</u>

Papaspyrides, C. D. et al., Athens University, 2002. https://doi.org/10.1002/app.11147



Blends with Elastane

Elastane is a polyurethane (PU) **commonly incorporated into blends.** It constitutes typically a minority fraction (<20%) but is increasingly prevalent in various textile compositions. The **cotton/elastane blend** is the most frequent bi-material blend after polycotton in the flows analyzed at sorting centers. [1].

Composition blend with elastane in outgoing streams from sorting facilities

Share of cotton/elastane: **4.9%** - Rank: **6**th Share of polyester/elastane: **1.3%** - Rank: **13**th Share of polyamide/elastane: **0.6%** - Rank: **19**th

Data from the Refashion characterization study [1], analysis of 14.6T (74,000 pieces) of non-reusable textiles.



Preferred chemical recycling routes?

Various methodologies for extracting elastane from blends are the subject of research:

Elastane dissolution & Hold other fibers

Objective: solubilize elastane in a solvent without dissolving/degrading other fibers

Elastane degradation & Hold other fibers

Objective: find an enzyme that selectively degrades elastane

Hold Elastane & Other fibers degradation

Objective: chemical or enzymatic depolymerization of the other fiber

$\sum_{i=1}^{N}$ Projects and research on the chemical recycling of elastane blends:





De Meester, S. *et al.*, Ghent University, 2023. <u>https://doi.org/10.1016/j.resconrec.2023.106903</u> Yi, C. *et al.*, Hunan Normal University, 2021. <u>https://doi.org/10.1177/0040517520931893</u> Review: Tonsi, G. *et al.*, Milano University, 2023. <u>https://doi.org/10.3303/CET23100122</u> Re:lastane, Qingdao Amino Materials Technology, 2022. Removing PU fiber from polyester, Teijin Frontier, 2023. <u>https://www.teijin.com/news/2023/04/10/20230410_01.pdf</u>



Chemical recycling of more complex blends (3 or more materials)

Mixtures of ternary or even quaternary materials make fiber separation and recycling very difficult, unless one material is highly predominant. These blends account for almost 9% of the non-reusable used textiles analyzed as part of the characterization study of sorting center outgoing flows [1]. The **most common is the cotton/polyester/elastane blend** (1.7% of non-reusable textile waste analyzed, by weight). Currently, there are no chemical recycling processes for these complex blends.



Summary

Non-reusable post-consumer textiles are complex to recycle for a variety of reasons: highly heterogeneous feedstock, variability of composition, blends of fibers and recycling disruptors (hard points, finishes, etc.). Product eco-design is therefore a key step in improving recyclability. The collection, sorting and feedstock pre-processing stages (trims removal, shredding, purification) upstream of recycling are also essential to ensure efficient recycling, whatever the route used.

Research on technologies for the chemical recycling of non-reusable used textiles has been progressing and accelerating in recent years. Depending on the material, different routes are being explored: **depolymerization (chemical or enzymatic)** to recycle synthetic material, and **chemical dissolution** to recycle and separate fibers in blends. The technologies developed mainly target cotton, polyester, polycotton blends and polyamide (PA 6). Some are now reaching maturity, and industrialization projects in France and Europe are underway.

These new chemical recycling technologies are promising, as they enable fibers to be broken down into their basic components, thus obtaining pure, colorless monomers/polymers, recovering properties equivalent to those of virgin polymers, recycling materials in a closed loop, specifically separating a material from a blend, or recycling fibers that are too degraded to be recovered by another recycling route. However, they also have their limitations, which vary from one technology to another: material purity is a key factor in recycling efficiency, and requires major upstream sorting and purification stages, sometimes high energy, water and chemical (solvents, catalysts, etc.) consumption, and still high costs (numerous stages and resources consumed). It is therefore essential to strike a balance between the technical advantages, environmental impact and economic viability of chemical recycling.

The development of chemical recycling technologies as a complement to other recycling routes should considerably increase the material recovery of non-reusable used textiles. The use of these new technologies will need to be assessed from an environmental and economic point of view, compared with existing mechanical or thermomechanical recycling alternatives.



Refashion's Recycle platform aims to bring together players in the Textile and Footwear Sector to accelerate the industrialization of the recycling of nonreusable textiles and footwear. Through the organization of workshops and

webinars, Refashion builds bridges between companies offering materials and the manufacturers who will incorporate them into their production processes.