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Recyclability of novel and sustainable energy harvesting and storage technologies for IoT and wireless sensor network

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European foreword

This CEN and CENELEC Workshop Agreement (CWA 18095:2024) has been developed in accordance with the CEN-CENELEC Guide 29 “CEN/CENELEC Workshop Agreements — A rapid prototyping to standardization” and with the relevant provisions of CEN/CENELEC Internal Regulations — Part 2. It was approved by a Workshop of representatives of interested parties on 2024-02-21, the constitution of which was supported by CEN and CENELEC following the public call for participation made on 2023-11-28. However, this CEN and CENELEC Workshop Agreement does not necessarily include all relevant stakeholders.

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Introduction

The Internet of Thing concept and demand for wireless sensor networks require efficient devices. Energy storage is crucial for these devices' functionality, often employing high-density, high-voltage lithium-ion batteries. Supercapacitors with new materials like polymer/carbon composites offer an attractive alternative for storing energy that coupled with lightweight Energy Harvesting Systems (EHSs) to collect energy from the environment, eliminate the need of conventional batteries, while reducing costs and environmental impacts. EHSs enable self-sufficient wireless sensor networks nodes operating indefinitely with an appropriate energy source. Promising devices combine energy harvesting and sensing, converting mechanical or thermal energy into electrical energy.

The InComEss project [1], as a part of the Horizon H2020 program, aimed at developing new green, cost-effective and highly efficient EHSs for feeding wireless sensor networks that can be used in IoT edge/cloud-based applications. Furthermore, circular economy principles were integrated to consider environmental impact, resource efficiency and material recycling.

This CWA, based on some of the results of the InComEss project, outlines a sustainable strategy by assessing the recyclability of EHS devices, identifying valuable materials that can be recovered as well as the different material recyclability solutions that could be applied.

1 Scope

This document compiles the techniques identified for the recovery of novel and high-value materials from end-of-life energy harvesting devices used for IoT and wireless sensor networks.

The CWA is applicable to recoverable materials and components considered of interest based on the design and composition of the Energy Harvesting Systems (EHSs) devices defined in this document: Polyvinylidene fluoride (PVDF), silver electrodes, polyimide, fiberglass/resin composite, copper, single walled carbon nanotube (SWCNT), polymeric matrices, aluminium, polyethylene terephthalate (PET) and carbon particles.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at <https://www.iso.org/obp/ui>
- IEC Electropedia: available at <https://www.electropedia.org/>

4 Abbreviations

For the purposes of this document, the following abbreviations apply.

Carbon Fibre Reinforced Composites	(CFRCs)
Depolymerized epoxy oligomer	(DEO)
Dimethyl phthalate	(DMP)
Dimethyl sulfoxide	(DMSO)
Dimethylformamide	(DMF)
Energy Harvesting System	(EHS)
Fatty acid methyl esters	(FAMEs)
Fibre Optic Sensors	(FOS)
Global Positioning System	(GPS)
Hydrogen fluoride	(HF)
Internet of Things	(IoT)
Micro Electro-Mechanical System	(MEMS)
N-methyl pyrrolidone	(NMP)
Piezoelectric generator	(PEG)
Polyaniline	(PANI)
Polyether ether ketone	(PEEK)
Polyethylene terephthalate	(PET)
Polyvinylidene fluoride	(PVDF)
Single walled carbon nanotube	(SWCNT)
Supercapacitor	(SC)

Tetrahydrofuran	(THF)
Thermoelectric generator	(TEG)
Waste Electrical and Electronic Equipment	(WEEE)

5 Energy Harvesting Systems configuration and application

The EHS described in this document is composed by generators lead-free piezoelectric composite strips/flat tapes-based mono-/bi-component fibres (Piezoelectric Generator: PEG) and innovative high-performance thermoplastic-based p-and n-type thermoelectric composites (Thermoelectric Generator: TEG) and as storage system for the harvested energy, a monolithic Supercapacitor (SC) developed with a printable high energy density PANI/carbon-based composite electrode. The full concept is depicted in Figure 1.

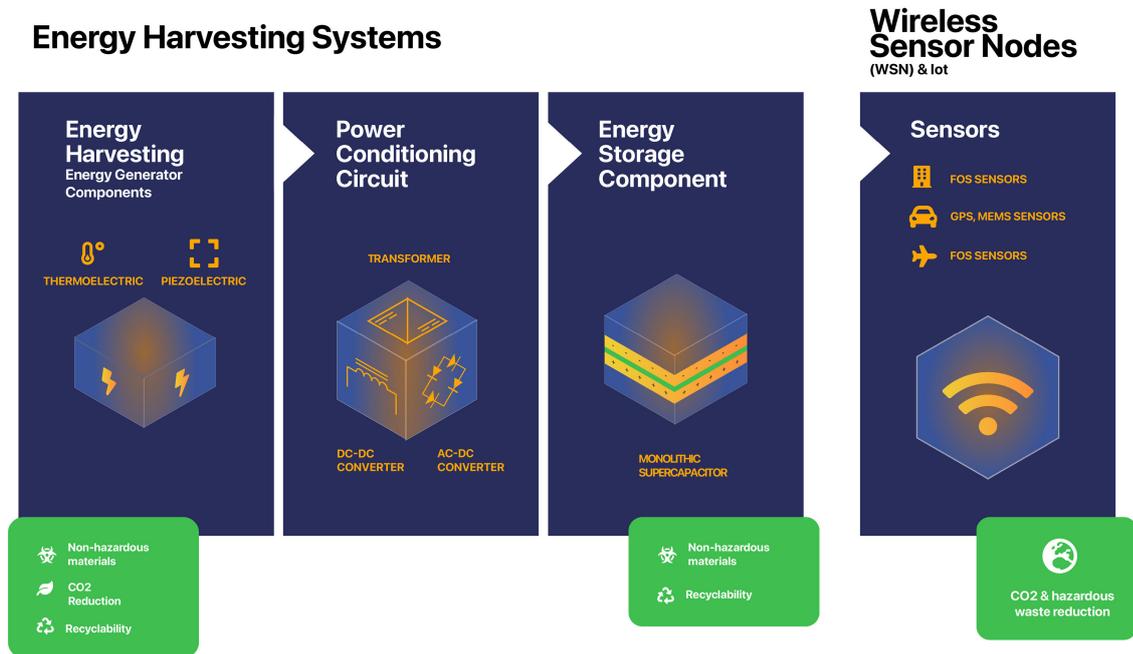


Figure 1 — Energy Harvesting Systems configuration

The system is used to power selected wireless sensor nodes to be implemented in different IoT scenarios for Structural Health Monitoring (SHM) in buildings and aircrafts (using a new miniaturized wireless Fibre Optics Sensing (FOS) interrogator with low power consumption) as well as wireless temperature sensors and accurate location and monitoring of MEMS (Micro Electro-Mechanical System) sensors in vehicles through Global Positioning System (GPS) and MEMS sensing.

6 Bill of materials and design of EHS devices

This clause describes the bill of materials of the EHS devices as well as their design, as a basis for the study of the recycling techniques.

6.1 Piezoelectric Generator design

In the case of PEG, the polyvinylidene fluoride (PVDF) is used as the main polymer for piezoelectric composites. This thermoplastic polymer is blended with a dispersing agent (organic additive). An extrusion-based technology is used for the manufacturing process of the strips as it is suitable for PVDF orientation. In this way, the polymer pellets are fed into an extruder consisting of a twin screw and a barrel for melting employing heat, and then, the

molten polymer is forced through the die and transformed into a long strip while it is quenched in water, becoming solid. In a second process, the strips are stretched to increase the crystalline beta-phase of PVDF and therefore, enhancing piezoelectric properties.

Using silver-based ink by screen printing, the electrodes are printed on each side of the stripes to be subjected to a polarization step (application of high electrical field). Once poled, the piezoelectric strips are cut according to the final design and bonded onto a fiberglass composite carrier beam using an epoxy resin as adhesive. Silver-based contacts are connected to the encapsulation layer through the copper electrodes, and the boards are glued with epoxy resin at the bottom and upper sides of the piezoelectric strip. Then, using epoxy resin this device adheres to the cantilever made of fiberglass composite. Two electrodes connect the strip's bottom and upper part using two wires. Figure 2 shows the PEG design based on PVDF tapes.

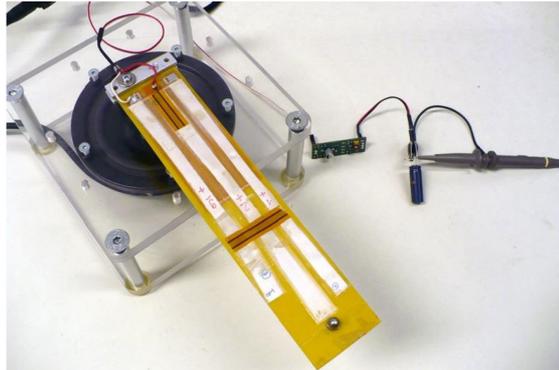


Figure 2 — PEG design

6.2 Thermoelectric Generator design

Since the main objective is to develop innovative high-performance thermoplastic-based thermoelectric composites with improved Seebeck coefficients for integration into a TEG for applications requiring a high temperature range ($-25\text{ }^{\circ}\text{C}$ to $+240\text{ }^{\circ}\text{C}$), the polymer selected and used as a matrix for the development of these thermoelectric materials is poly (ether ether ketone) (PEEK), a high-performance thermoplastic polymer.

The design of the TEG is based on a combination of p-type (most charge carriers are electrons) and n-type (holes are the dominant charge carriers) materials. Thermoelectric composites are essentially produced by the melt compounding method in which the polymer matrix is melted, and single-walled carbon nanotubes (SWCNTs) are incorporated as conductive fillers under shear action into the molten matrix at concentrations less than 3 % weight for the case of p-type compounds. To obtain n-type compounds, polyethylene glycol is used as a shift additive (at concentrations of around 15 % weight) to induce a negative Seebeck coefficient (p- to n-type shift). As a result of the melt mixing process, composite strands are obtained. These strands are then formed into sheets through the hot compression moulding process. According to the final design of the generator, plates of p- and n-type PEEK composites are compression moulded and then strips of the required dimensions that form the legs are cut from them. More explanations about the material production process are given in [2]. The P and N type legs are connected by sputtering with copper foil or conductive silver paste. In the case of a block design, this assembly is embedded in an epoxy resin to stabilize the geometry (see Figure 3). This design allows the TEG to be exposed to cold on one surface and heat on the other.

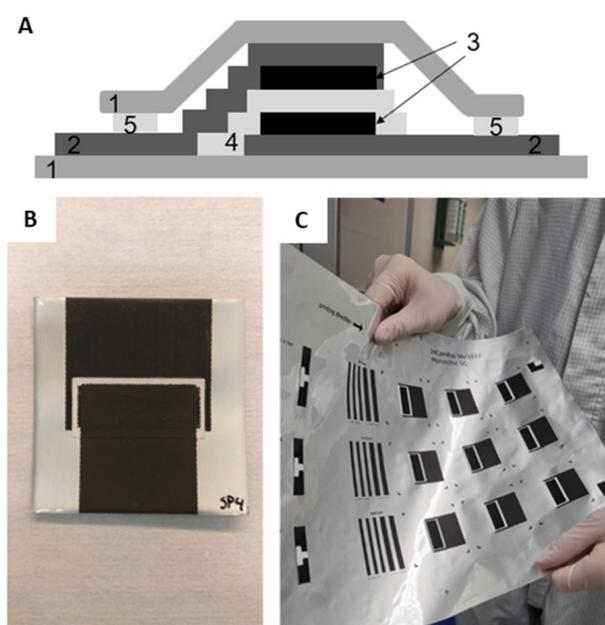


Figure 3 — TEG design

6.3 Supercapacitor design

The design of the printed monolithic supercapacitor is represented in Figure 4. A PET/aluminium laminate is used as a substrate for its construction. The total thickness of the substrate and encapsulation (element 1) is 60 μm , with the thicknesses of the individual PET and aluminium layers being 50 μm and 10 μm respectively. In this structure, aluminium acts as a barrier layer. The current collector (element 2) is made from Henkel Electrodag PF407C conductive ink, a graphite filled composite that is cured at high temperatures (90 °C-120 °C). The electrode (element 3) consists of a water-based PANI/carbon ink, made by mixing chitosan binder with active material powder composed of PANI/carbon composite synthesized through in-situ chemical oxidative polymerization of aniline and carbon with ammonium persulfate as oxidant. The separator (element 4) is a talc-cellulose-chitosan (20:5:1 mass ratio) mixture. Finally, the electrolyte is a 0,5 M Na_2SO_4 . To ensure the sealing of the device within the encapsulant layers, the 3M 468 MP acrylic adhesive (element 5) is used around the electrode area.

Figure 4A shows the schematic structure of the SC with all elements while Figures 4B and 4C show the screen printed monolithic SC and screen printed sheet of SCs together with different test patterns, respectively.



Key

- 1 PET/Al (substrate + encapsulation)
- 2 Current collector
- 3 Electrode
- 4 Separator
- 5 Adhesive

Figure 4 — SC design

The weight fraction of all components is provided in Table 1.

Table 1 — SC composition

Component	Material	Weight percentage (%)
Encapsulation & substrate layers	PET	53,0%
	Aluminium	20,5%
Current collector	Graphite particle	3,3%
	Thermoplastic matrix	2,2%
Electrode	Activated carbon particle	0,2%
	Chitosan/PANI matrix	2,1%
Separator	Talc	2,8%
	Cellulose	0,7%
	Chitosan	0,1%
Adhesive	3M 468 MP tape	11,6%
Electrolyte	0,5 M Na ₂ SO ₄	3,5%

7 Consideration on the devices end of life

The design of an integrated EHS should consider the repairability and separability of its devices (PEG, TEG and monolithic SCs) from the system and the application. This is important because the expected lifespan of the device may be different from that of its many possible applications.

The expected lifespan of the EHS should be compared with the lifespan of its individual devices and the lifespan of the application it will be used in. For instance, when considering a possible application in the automotive sector for a light-duty vehicle, a lifespan of around 10-15 years is expected, while for applications in the construction sector such as buildings the expected lifespan is much longer, around 80-100 years, and in the aeronautical sector an aircraft is estimated to have a 20–30 year span. This comparison is essential in determining the sustainability of the device over its lifetime.

Detachability from the application is a crucial sustainability factor to be considered. If the device is not removable, such as if it is embedded, it will apply the End-of-Life (EoL) of the application and its waste stream. This would mean that the device's EoL is determined by that of the application. On the other hand, if the device is removable, it is considered the preferred option since the device will determine its EoL and its waste stream.

Therefore, it is important to design the devices considering their bill of materials, recoverability and recyclability of valuable materials and waste minimization.

7.1 Expected waste streams and recycling route

Given the characteristics and potential detachability of these devices, it is expected that the most likely route they will take at the end of their life is the Waste Electrical and Electronic Equipment (WEEE) stream. The configurations described in clause 6 make possible to argue that the processes used in established industrial WEEE treatment facilities are not adequate for the recovery of valuable materials from these PEG, TEG and SC devices. Therefore, the nature of these devices, which are based on a polymeric compound, especially for PEG and TEG, may drive the search for the best recycling techniques towards the recycling of polymeric composites comprising mechanical and thermal (pyrolysis, fluidized bed pyrolysis and microwave pyrolysis) and chemical-based approaches (solvolysis) [3].

8 Recoverable materials

Before getting into the different recycling techniques for the EHS devices, each device shall be evaluated according to its design to define which high-value materials could be recovered.

This subclause indicates the different recoverable materials that can be obtained from each device.

8.1 Piezoelectric Generator

Considering that the PVDF piezoelectric strips bonded to the surface of the cantilever of the PEG can be removed from the devices without damaging them, the products to recover would include PVDF, together with the silver electrodes that are joined to the PVDF strip in the cantilever design, polyimide (from Kapton®), fiberglass/resin composite and copper. It is important to clearly define the separation way of the piezoelectric strips from the cantilever to extract the PVDF in good conditions.

8.2 Thermoelectric Generator

TEGs are primarily made up of polymeric matrices, with PEEK being a thermoplastic known for its exceptional properties. PEEK is chosen for its high thermal stability (up to 240 °C) required for the application. It acts as a host for SWCNTs and polyethylene glycol in a thermoplastic nanocomposite. While the ideal recycling efficiency for TEGs is 100 %, SWCNTs hold the highest value in the device, contributing to over 90 % of the costs despite their small percentage. According to the market, SWCNT (3000 €/kg) shows the highest cost per kilogram in comparison to PEEK (52 €/kg) or polyethylene glycol (60 €/kg). Recovering SWCNTs during recycling is challenging due to their complex isolation from the polymeric matrices. For this reason, the recoverable materials from TEGs would be the polymeric matrices, along with the SWCNTs, that can be reused for producing new TEG components or other applications.

8.3 Supercapacitor

According to the design of the SC, the most valuable material from the substrate and encapsulation layer is aluminium although improved device design in the future could reduce the foil thickness from the current 10 µm to 100 nm, making it difficult and potentially unsuitable for recycling. Aluminium is a critical raw material that is widely used in various industries. Additionally, found in the substrate and encapsulation layer, PET represents more than half of the weight of the SC, and its recovery and valorisation should also be considered. Recycled PET cannot be easily introduced into food packaging due to concerns about residues or contamination, but it can be valuable and applicable in the textile industry [4]. Both electrode and current collectors contain carbon particles. The recovery and reuse of these carbon particles from the electrodes and current collectors can also be considered although their low weight fraction makes it challenging to achieve a reasonable recovery rate.

However, Na₂SO₄ is a common by-product of several industrial processes and is often considered a hazardous waste. The talc, main component of the separator element, is a cheap and common material, so its recovery is not considered. PANI and chitosan are also not considered as recoverable material due to their low weight percentage and low economic value. The acrylic adhesive makes up about 1/3 of the weight of the SC, but as it is classified as a Group 7 plastic¹⁾, it is difficult to recycle.

9 Recycling techniques

This clause describes the recycling techniques available for each device considering the recoverable materials identified above.

9.1 Piezoelectric generator

The first consideration to take into account in PEG is the degradation of the encapsulation layer. Epoxy resin is a type of thermosetting plastic difficult to melt and reshape. However, there are mechanical, thermal and chemical techniques that can be used for its recycling. Chemical processes present an important challenge

1) ASTM D7611-20: Resin Identification Code Standard.

considering the potential effect on other target components. Mechanical recycling by crushing would result in a mix of crushed composites that could be used as reinforcement pieces [5].

Epoxy resins can be removed by combining heat and pressure exposing the material to temperatures above its softening point. In this way, the adhesive softens and the components can be de-bonded. Temperatures of about 400 °C or higher will degrade the resin, allowing separation of the components as well. However, the integrity of the PVDF strips can be affected hindering their recycling. It is proposed to treat the encapsulation layer by microwave assisted degradation with Tartaric acid and hydrogen peroxide (H₂O₂, 50 % weight). This method would allow to decompose the epoxy resin and release the piezoelectric strips. The use of an organic solvent such as NMP (N-methyl pyrrolidone) in a microwave assisted degradation at 80 °C would also be an option, however, it is not clear how this treatment would affect the physicochemical properties of the PVDF strips.

The boards composed of fiberglass and epoxy resin can also be recovered whole and destined for reusing in electronic components. For recycling the composite, it could be dissolved using acids, alkalis, alcohols, or water to produce fibres and monomers.

Once the encapsulation layer has been degraded, the main recoverable materials from PEGs include: PVDF, Polyimide, silver, and copper. The available treatments to target each of these materials are described below:

- **PVDF**

Recycling of fluoroplastics such as PVDF is economically attractive due to their high stability and value. In general, recycling of PVDF has been studied and reported in the framework of lithium-ion battery treatment, where it is found as a polymeric binder, demonstrating that more research is needed on the recycling of PVDF recovered from other waste streams.

Recycling PVDF can be a challenge due to its high resistance to chemical and mechanical degradation processes. Different recycling techniques are being researched:

- **Chemical treatment:** The low chemical reactivity of PVDF challenges solvolysis. [6] presents a summary of effective solvents and diluents for PVDF recovery including acetone, DMF (dimethylformamide), DMP (dimethyl phthalate) and supercritical fluids. In [7] the use of organic solvents including DMF, NMP and THF (tetrahydrofuran) is evaluated. Addressing the use of greener solvents, a study by [8] evaluates the use of a bioderived solvent Cyrene® (dihydrolevoglucosenone) which proved to be effective at temperatures higher than 80 °C allowing for PVDF recovery by precipitation at lower temperatures.

The use of supercritical CO₂ combined with DMSO (dimethyl sulfoxide) as a cosolvent is reported in [9] having achieved a 98,5% weight recovery of pure PVDF from lithium-ion battery cathode in 13 minutes under a pressure of 80 bar at 70 °C. Other solvents studied include fatty acid methyl esters (FAMES) and ionic liquids, however, these are expensive and therefore an economically unviable option. New technologies for PVDF degradation include the combined use of molten salts and high voltage discharges.

- **Thermal treatment:** At room temperature, PVDF does not easily corrode in the presence of acids, strong oxidizers or even halogens. Additionally, suitable solvents are hazardous, so the development of thermal processes has been evaluated.

The major challenge in recovering PVDF by thermal decomposition is the production of fluorinated organic compounds such as fluorobenzene and HF (hydrogen fluoride) which could lead to environmental pollution. Direct calcination can result in the emission of these pollutants, being pyrolysis in a completely closed environment a better processing option with full control and possibility of treatment of the exhaust. [10] reports an optimum pyrolysis temperature range between 500-580 °C.

Under moderate alkalinity conditions, PVDF can be recovered without undergoing defluorination or physical deterioration. The use of ammonia has been shown to be effective in eliminating dioxin generation in high temperature dehalogenations. [11] proved PVDF did not deteriorate in a process carried out at 100 °C for 2 hours at 10M NaOH. However, the high corrosiveness of inorganic fluoride directly hinders the lifetime of the equipment by increasing costs.

— **Mechanical treatment:** PVDF can be recycled as a thermoplastic through extrusion re-melting. Despite scarcity of reports on the use of mechanically recycled PVDF, [12] compared a reference sample to two recycled samples. They concluded that no major changes of PVDF properties were observed after extrusion, making mechanical treatment as a viable recycling option.

• **Polyimide (Kapton®)**

The recyclability by reuse of polyimide thermoplastics such as Kapton® is between 5-8 %, leaving the remaining 92% under an unclear problem to solve.

The recycling techniques researched are indicated below:

— **Chemical treatment:** Hydrolytic degradation and water-induced plasticization is an environmentally sound method, but highly dependent on time (month scale) and energy as it requires thermal activation. Hence, chemical treatment is combined with mechanical processes to achieve more effective and efficient recycling. For instance, the advantages of ball milling have been recently demonstrated. Ball milling is a simple process, economically viable and perceived as a greener option than chemical recycling. In this way, high purity starting monomers and partially imidized powders in a metastable state are obtained.

— **Thermal treatment:** Oxidative degradation of polyimides starts at 350 °C. Subjected to thermal degradation, Kapton® generates mainly CO₂, CO and other volatiles. Pyrolysis can be used to produce reticulated structures such as microporous membranes to applied as gas filters [13].

— **Mechanical treatment:** Products such as Kapton® can also be reused. By applying ion etching, [14] developed patterned through-holes on the film which, combined with the intrinsic electrostatic forces from Kapton®, provide the capacity to efficiently capture particles ranging from 0.3 μm to 10 μm in long-term dust filtration.

• **Metals: Copper and Silver**

In PEGs, the polyimide component contains copper, so the method selected to recover this metal will depend on that selected to recycle the polyimide. Consequently, copper can need to be recovered from pyrolysis ashes or by acid leaching of the recovered polyimide. It can also be necessary to evaluate the effect of this metal on the product obtained from Kapton® recycling considering its aimed purpose.

On the other hand, silver electrodes are soldered to PVDF strips, thus their recovery will depend on the treatment chosen to recover PVDF. Silver-based contacts can be recovered manually.

Finally, the silver-based ink used to print the PVDF strips requires further research to determine how it interacts with the selected method and products.

Table 2 shows a summary of the possible recycling techniques for the PEG:

Table 2 — Recycling techniques selected for the PEG

Components	Composition	Recycling techniques	Recoverable materials
Encapsulation layer	Epoxy resin + Fiberglass	Microwave assisted degradation with Tartaric acid H ₂ O ₂	Piezoelectric strips
	Polyimide + printed copper	Milling in high-energy ball mill	Polyimide powder
		Pyrolysis at T>300 °C	CO ₂ together with CO and other volatiles
Piezoelectric film	PVDF	Dissolution: a. Propylene Carbonate b. Dihydrolevoglucosenone	Membrane casting Gel formation NOTE: An evaluation of the effects of the presence of silver-based ink should be performed
Electrodes	Copper	Dependent on method selected for recycling the polyimide	Copper compounds
	Silver	Dependent on treatment chosen to recover PVDF. Silver-based contacts: manual recovery. Silver-based ink: further research required	Silver contacts

9.2 Thermoelectric generator

- **Sputtered copper connections**

In the case of the TEG, the sputtered copper connections can be recovered through recycling techniques such as manual sorting, mechanical processing, pyrometallurgical recycling, hydrometallurgical treatment and electrolytic recycling. In the particular case of hydrometallurgical treatment, the sputtered copper connections can be separated by subjecting them to nitric acid (3M) at 60 °C for 5 hours and a pulp density of 25 g/L. The copper can then be extracted as copper hydroxide (II) by adjusting the solutions pH to 6 using a 0,5 M sodium hydroxide solution.

- **Epoxy resin**

Different techniques can be applied for recycling epoxy resin:

- **Mechanical treatment:** The mechanical recycling of the TEG assembly by crushing would result in a mix of composites containing epoxy resin, p-type (PEEK/SWCNTs) and n-type legs (PEEK/SWCNTs/Polyethylene glycol). These composites can be used as reinforcement pieces for other materials [5] but it is likely that their composition is not uniform, making this application difficult. Another possibility is the application of cryo-shredding followed by a materials separation stage based on their different sizes and/or densities. This process is based on epoxy being quite brittle, while the polymer parts are more flexible and should result in larger shredder sizes.

- **Thermal treatment:** Other recycling technique is pyrolysis. For this technique, the presence of different components in the sample (epoxy resin/PEEK/SWCNTs/polyethylene glycol) should be considered to correctly estimate the behaviour of the materials during the thermal treatments. The anaerobic (nitrogen atmosphere) and oxidative pyrolysis until 800 °C of epoxy resin reinforced with carbon fibres has been reported in [15]. The liquid fraction of both types of pyrolysis was composed of methylcyclohexene and phenolic derivatives, whose concentration was lower for the oxidative pyrolysis. The gas fraction from the anaerobic pyrolysis mainly contained CO₂, CH₄, H₂ and H₂O, and from the oxidative pyrolysis, CO and CO₂. The pyrolysis of PEEK under inert atmosphere (He) to 900 °C showed two regions: (1) up to 650°C ether group and ketone group decomposed to phenol and CO₂ and the fluorenone structure moved to the carbonization scheme; (2) until 900 °C the ketone group of fluorenone and from the carbonized structure decomposed to CO₂. However, the thermogravimetric analysis of SWCNT in inert atmosphere shows the SWCNTs burning at 765 °C. Thus, the anaerobic pyrolysis of the TEG would result in a liquid fraction made of methylcyclohexene and phenolic derivatives and a gas fraction made of phenol, CO₂ and CH₄. As SWCNTs, the most expensive materials in TEGs, would not be recovered, it can be concluded that this method is not suitable for TEG recycling.
- **Chemical treatment:** Also known as solvolysis, it has been broadly studied for the epoxy resin recycling. This technique comprises the transformation of the resin into monomers, oligomers or other substances through the addition of solvents under certain reaction conditions (i.e., residence time, pressure, temperature, catalyst, pulp ratio, agitation).

When using a chemical recycling method, special attention shall be paid to the sputtered copper connections, as these connections on the surface of the polymer-based strips can also be de-bonded and separated.

Chemical recycling of the epoxy resin composites containing resin and carbon fillers can be pursued to depolymerize the resin and release the thermoelectric legs. It is expected that this method does not damage the PEEK due to the difficulties found to depolymerize this molecule. In this way, temperatures higher than PEEK melting point (345 °C) are requested for the PEEK solvolysis. [16] reports on the use of bond exchange reaction assisted by small molecules in a mixed solvent of dimethylformamide/ethylene glycol (50/50). At a later stage, depolymerized epoxy oligomer (DEO) and the solvents are separated by distillation. It has been also demonstrated that this method would be applicable for the recycling carbon fibre reinforced composites (CFRCs) recovering high-value carbon fibre. The decomposition of bisphenol F-type epoxy resin and typical amine curing agent to picric acid is performed using 4 M nitric acid at 80 °C for 30h. Increasing the nitric acid concentration to 7,1 M and working at 60 °C the residence time is reduced to 30 min. Epoxy resin can be 99% degraded using supercritical water. Working with phenolic resins, phenol and KOH in subcritical water allows a decomposition efficiency of 95,2%. Super- and subcritical alcohols and mixed systems, such as methanol, ethanol, n-propanol, iso-propanol, n-butanol and acetone, and/or KOH as catalyst, can be also used for the epoxy resin degradation. The highest degradation efficiency using these systems is 97,6%. The use of peracetic acid generated in situ from a mixture of acetic acid and H₂O₂ to oxidize the epoxy resin reached degradation efficiencies of 97% at 65 °C for 5 h. Total degradation of thermoset epoxy resin can be achieved using a combination of ionic liquid and alcohol (1-butyl-3-methyl imidazolium chloride and ethylene glycol) at 150 °C in 2,5 h under atmospheric pressure.

- **Thermoelectric legs or leg materials**

In the case of thermoelectric leg materials from TEG, two different aspects can be considered, their reuse and their recycling.

- **Reuse:** Once the thermoelectric legs have been recovered intact, they may be directly reused in a similar TEG application. This requires that the dissolving of the epoxy embedment could be done in a suitable way without any dimensional, physical or chemical damage of the thermoelectric legs.

The thermoelectric legs or their shredded granules should be treated by a melt processing step to obtain reusable materials (PEEK based SWCNT composites) with the desired properties. This can be done by melt-compounding, e.g. in an extruder, under addition of the additive polyethylene glycol (if n-type material is aimed) or by adding somehow more SWCNTs to reobtain the initial properties. [17] explains the

production process of n-type legs based on SWCNTs and PEEK; accordingly, the recycled PEEK composites could be reused as an input to feed the main hopper of the compounder. This type of treatment has been already done on carbon fibre-reinforced PEEK. The end-of-life polymers are grounded and added to virgin PEEK, conferring to the material even better mechanical properties. However, no references have been found regarding the reuse of thermoelectric polymers based on CNT/PEEK composites.

- **Recycling:** The p- and n-type leg materials could be also recycled to obtain SWCNTs and PEEK separately. However, the decomposition of PEEK requires extreme conditions such as working in sub- and supercritical water system using Na_2CO_3 as catalyst at 703 K during 3 h for reaching a yield of 88%. 2-phenylethanethiolate is also used as a reagent for an effective depolymerization of PEEK (yield equal to 98%), followed by treatment with organic halides, but further research must be done on this field for optimizing the reaction conditions and processing times. Moreover, the acid treatment of PEEK becomes very complicated as this polymer is insoluble in all common solvents except strong acids such as 98% sulphuric acid and hydrofluoric acid, which are not recommendable due to health hazard, toxicity, corrosive properties and other potential risks. The thermal treatment was explained above, leading to the conclusion that it is an unsuitable recycling technique.

Table 3 shows a summary of the possible recycling techniques for the TEG:

Table 3 – Recycling techniques selected for the TEG

Components	Composition	Recycling techniques	Recoverable materials
Terminals	Copper	Hydrometallurgy: nitric acid 3 M at 60 °C	Copper hydroxide
Casing + p-type leg & n-type leg	Epoxy resin, [PEEK + SWCNT] & [PEEK + SWCNT + Polyethylene glycol]	Mechanical	Reinforcement for composites
		Pyrolysis	Methylcyclohexene and phenolic derivatives, phenol, CO_2 , CH_4 with a small amount of C_2 and C_3 gases
Casing	Epoxy resin	HNO_3 7,1 M / 60°C / 30 min	Functional chemicals
		Supercritical fluid water / 150 °C / 10 min	Phenol-like chemicals
		Dimethylformamide/ethylene glycol (50/50) / 150 °C / 30 min	Depolymerized epoxy oligomer
		Subcritical water / phenol / KOH / 315°C / 30 min	Monophenolic, bisphenolic and amine compounds
		Peracetic acid / acetic acid / H_2O_2 / 65 °C / 5 h	Oxidation products of amine-cured epoxy resin, higher molecular weights compounds
		1-butyl-3-methyl imidazolium chloride and ethylene glycol) at 150 °C / 2,5 h	Alcohol derivative of the Bisphenol A Dglycidyl ether
p-type leg & n-type leg	[PEEK + SWCNT] & [PEEK + SWCNT + Polyethylene glycol]	Mechanical treatment	Crushed PEEK / SWCNTs composites
		Supercritical water / Na_2CO_3 / 430 °C / 3 h	Monomers such as phenol, cresols, and their analogues
		2-phenylethanethiolate + treatment with organic halides	PEEK monomer

9.3 Supercapacitor

The supercapacitor consists of layered polymeric systems. Recovering materials from the SC can be approached in two ways: separating each component individually or treating the SC as a single polymeric system to recover all materials together. Both methods involve mechanical, thermal, and chemical processes, though there may be compatibility, process overlap and performance efficiency issues in the latter approach.

- **Separation of components**

Mechanical pre-treatment like trituration can expose components for further processes. However, processing and separating materials from the resulting mixture can be challenging. Thus, chemical and/or thermal treatment may be more viable options.

Chemical pre-treatment with solvents can break bonds between printed layers and separate components. However, solvents could have different effects on PET, PANI, and chitosan making further separation of PET infeasible. Thermal pre-treatment can remove sealant and separate the top Aluminium/PET layer. Complete degradation of PET, chitosan, PANI and the current collector adhesive can be achieved at around 500 °C, allowing for easy separation of aluminium.

- **Aluminium and PET**

- **Chemical treatment:** Various recycling techniques have been proposed for the separation of aluminium and PET layered polymers from waste cardboard packaging for beverages and food or pharmaceutical blister packaging. Among them are electromechanical separation and electrohydraulic fragmentation, although with not very efficient results. More effective chemical methods to leach aluminium using hydrochloric acid, sodium hydroxide or bioleaching with bacteria has been proposed. Solvents can be used to dissolve the polymer, with organic solvent such as mixture of benzene, ethanol and water or with more environmentally friendly deep eutectic solvents. Phenol has been demonstrated to be able to dissolve waste PET bottle as well as trifluoro acetic acid and trichloro acetic acid and hexafluoro-2-propanol. The recovery performance depends on the polymer and solvent polarity. Other PET depolymerization methods can be used, such as hydrolysis, methanol alcoholysis, ethylene glycol alcoholysis, alcohol-alkali combined depolymerization or ammonolysis. Another promising chemical technique using sub- and supercritical water can recover all aluminium in solid form without oxidation. In any case, solvent reusability and impurity removal need to be addressed before implementing these techniques in industry.

However, these chemical processes need to be assessed for the SC to verify dissolution of other components such as PANI and chitosan. (18) reports that PANI is infusible and insoluble in conventional solvents. PANI usually exists in a powdery form and forms fine colloidal suspensions rather than being solubilized. Chitosan can usually be dissolved in strong hydrochloric acid and weak carboxylic acids like formic acid, acetic acid and propionic acid while it exhibits low solubility in water and most organic solvents. Talc is practically insoluble in water, dilute mineral acids and dilute solutions of alkali halides and alkaline hydroxide while it is soluble in hot concentrated phosphoric acid.

- **Thermal treatment:** Thermal treatment can release valuable materials or separate components for further processes. PET melts above 250 °C, and according to thermogravimetric analysis curves, effective loss of mass (up to around 75%) happens between 400 °C and 450 °C. Chitosan cannot withstand temperatures above 220 °C and experiences a mass loss of up to 90 % at 600 °C. Crosslinked PANI has a glass transition temperature of around 250 °C with the greatest mass loss (usually around 80%) at 500 °C. The acrylic adhesive would begin to degrade above 210 °C, and slightly above this temperature the aluminium/PET layers could be separated from the rest of the device. This would allow the aluminium/PET layers to be treated separately as described above, leaving the rest of the components to undergo additional thermal treatment. In any case, a thermal treatment at 500 °C could easily release a clean layer of aluminium.

Other thermal processes such as pyrolysis, plasma or microwave-assisted pyrolysis recover polymeric parts in the form of oil or wax, which can be used as fuel or industrial feedstock and eventually used to support the pyrolysis process. Talc is expected to remain unchanged since the decomposition of talc begins at around 800 °C, peaking at 895 °C approximately, with the formation of enstatite and amorphous silica.

- **Carbon and graphite particles**

As previously stated, after either a chemical or thermal treatment, the aluminium is detached and removed, and the PET is possibly recovered or decomposed. The solid residue is a mixture of talc, carbon particles from the electrode and current collector, and residue from decomposed polymers. Solid residue from PET calcination usually lead to a mixture of aromatic acids and alkenes compounds. The challenge is the separation of the two carbon particles. Froth flotation techniques, even though they require quite large amounts of material to be effective, could be a suitable way to separate the carbon particle from the rest, separating the graphite from low-grade mineral materials.

Table 4 shows a summary of the possible recycling techniques for the SC:

Table 4 — Recycling techniques selected for the SC

Component	Composition	Recycling techniques	Recoverable materials
Whole SC	Aluminium/PET, adhesive, current collector, separator + electrode	Mechanical pre-treatment	Mix of crushed composites
		Thermal pre-treatment: 250 °C to break the 3M acrylic adhesive and release the encapsulation layers	Aluminium/PET layer
		Thermal pre-treatment: 500 °C	Aluminium
		Chemical pre-treatment	Separated SC layers
Substrate + encapsulation layer	Aluminium/PET layer	Electromechanical separation - previous trituration	De-bonded components: PET - Aluminium
		Electrohydraulic fragmentation and separation	De-bonded components: PET - Aluminium
		Hydrometallurgical processes	Aluminium + solid residual (PET)
		Dissolution of PET using solvents and diluents: organic solvent; deep eutectic solvents; phenol; trifluoro acetic acid and trichloro acetic acid; Hexafluoro-2-propanol; hydrolysis, methanol alcoholysis, ethylene glycol alcoholysis, alcohol-alkali combined depolymerization or ammonolysis; sub- and super-critical water	De-bonded components: PET - Aluminium
Current collector	Graphite particle + Thermoplastic matrix	Froth flotation	Graphite particle
Electrodes	Activated carbon particle + chitosan + PANI	Froth flotation	Activated carbon particle

9.4 Most suitable recycling techniques

Based on the identification of the most valuable recoverable components and materials of each device and the analysis of the different available recycling techniques, the following methods are identified as most appropriate:

For the PEG, the thermal and chemical stability of the components makes the definition of methods for their recovery and recycling complex. *A priori*, to recycle the encapsulation layer the most suitable methods include microwave assisted degradation of the epoxy composite and pyrolysis of the polyimide. Furthermore, dissolution

of the piezoelectric film using a green solvent appears to be a viable option. At a later stage, recovery of silver and copper would need to be defined according to the results obtained for the rest of the components.

In the case of TEG, the main issue comes from the use of PEEK. This polymer exhibits excellent mechanical strength, thermal stability and chemical resistance. In this way, it becomes very difficult to attack this polymer to deliver the SWCNT, which are the most expensive material within the TEG. For this reason, the best approach seems to be, firstly, the release of the thermoelectric legs via solvolysis of the epoxy resin where they are embedded. This can be done with inorganic acid, such as nitric acid at high concentration and temperature. Secondly, the thermoelectric legs can be mechanically treated and used as fillers for PEEK matrices, such as new thermoelectric devices or other applications based on reinforced polymers.

The main materials of interest for recovery in SC are aluminium, PET and carbon particles. Aluminium, despite its value, may become difficult to recycle in the future development of 3D printed SC due to tendency to reduce the thickness of aluminium foil. PET, a significant component of SCs, has the potential for recovery and valorisation. Carbon particles from electrodes and current collectors can be considered for recovery, although their low weight fraction poses challenges. Various methods have been proposed for material recovery, including mechanical, thermal and chemical treatments. Chemical treatments involving solvents show promise for separating components, but compatibility issues with PET, PANI and chitosan polymer need to be addressed. Thermal treatments can release valuable materials and pyrolysis/calcination processes offer the recovery of polymeric parts as fuel or feedstock. The challenge lies in the separation of carbon particles, which could potentially be achieved through froth flotation.

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