Science Arts & Métiers (SAM)
is an open access repository that collects the work of Arts et Métiers ParisTech researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: https://sam.ensam.eu
Handle ID: .http://hdl.handle.net/10985/12095

To cite this version:

Any correspondence concerning this service should be sent to the repository Administrator: archiveouverte@ensam.eu
ABSTRACT
This paper proposes a framework that interrelates the life cycle of the product, remanufacturing and recycling for plastics. The paper analyses the different chemical processes of recycling polymer wastes. We introduce a thermodynamic calculation of the energy consumed and CO2 emissions for all types of waste (municipal, electronic, vehicle). The remanufacturing process could reduce the amount of CO2 emissions through feedback to the product design stage with robust platforms that extend the product life cycle. In order to meet the requirements of remanufacturing we combine mechanical and chemical recycling solutions. These recycling processes must undergo a thermodynamic analysis to optimize energy and decrease the minimum CO2 emissions, i.e. recycling processes in line with the ultimate objective, which is the reduction of CO2 emissions and slowing a part of the problem global warming.

KEYWORDS
Recycling, polymer, thermodynamic, CO2 emissions

1. Introduction
Today designers have to take into account indicators related to environmental impacts of the products during their whole life cycle. From the cradle (raw material extraction) to grave (end of life of the product), all the impacts of the life phases of the product are evaluated. These impacts and emissions evaluations (such as CO2, energy or water consumption, etc) help designers to select and develop eco-designed products. End of life (EoL) of the products becomes a major question due to the needs of material efficiency (meaning saving and recycling a lot of materials when the product is at its end of life). Closing the material loop and circular economy perspectives are the today solutions for the product and its related organization development.

In order to improve the design for End of Life, recycling solutions has to be evaluated and
sometime to be developed. The integration, within the designer environment, of this topic needs to have a set of EoL’s solutions figures. This analysis gives also the opportunity to improve these solution and eco-design their processes. One option relies on integrating renewable energy into the recycling technology development. This is the goal of this paper. Data bases of recycling processes or recycling functional unit descriptions could give opportunities to have early evaluations for the EoL impacts, into the product development process. Other EoL alternatives, such as re-use or remanufacturing of components, are not taken into consideration into this paper, even if these solutions have a very positive impact on the environmental profile of the products at their EoL.

The current process used for the processing and industrial recycling of polymers to manufacture packaging, packaging and engineering plastics in the automotive and electronics industry uses fossil fuel energy. The fossil fuels used in burning, biomass burning, cement manufacturing, and changes in land use (mainly deforestation) are generating CO2 gases. These gases are trapping an increasing proportion of terrestrial infrared radiation and the global temperature is expected to increase 0.3 to 0.4°C per decade (so-called greenhouse effect and global warming) [1-7]. Consequently, improvements should be made in plastic product design and manufacturing (integrating recycled materials and actions taken to reduce manufacturing impacts). The end of life has to be improved (in terms of efficiency of recycling but also collection and use) and must also be analyzed from the CO2 and energy consumption perspective.

This paper presents a unified scheme of the product life cycle and interaction with recycling and remanufacturing. Remanufacturing (or even better re-use) is an important process for reducing CO2 emissions. This work emphasizes the need to design life cycle products that can be prolonged by remanufacturing the product. The paper also analyzes the existing processes for recycling plastics by an energy-ecological approach in order to optimize these processes and reduce CO2 emissions dramatically.

2. Life cycle, remanufacturing and recycling interaction

The life cycle of materials is a function of design and technological progress in the market. Unfortunately, in recent decades the design approach has tended to be one of short durability in order to maintain consumption and production flows. The volume of waste has increased tremendously and is now a major global problem. Many countries have cultural levels of consciousness for environmental awareness and litter. However, when all garbage, both organic and inorganic, is discarded in a single container, it creates pockets of infection and logistical problems in collection, transportation and separation of these wastes. This means increased consumption of energy and therefore more CO2 emissions compared to countries with a culture based on awareness of the environment. The consumer becomes the first link in the recycling chain, separating the different types of waste (paper and cardboard, glass, metals, plastics, food, green waste). This single action on the part of the consumer saves millions of tons of energy and reduces CO2 emissions considerably because there is specialized transportation taking each type of waste (glass, metal, papers, plastic) directly to appropriate recycling centers. Otherwise, when garbage is not separated, it goes to a collection centre, where separation is carried out by industrial machinery which uses a large amount of energy (mainly electricity), water and surfactants to pre-wash and separate. Total energy consumption and CO2 emissions increase, as well as the need to install a water treatment plant for sludge generated due to organic waste.

The valorization of plastic consists of burning, with some organic materials, in order to generate power used in heating the cement industry or to produce
steam to generate electricity. Again, this means a great generation of CO2 emissions, not to mention other polluting gases. Circular economy and cradle to cradle approaches need interaction between the product life cycle and end of life processes, with and without environmental culture. Recycling, remanufacturing or refurbishing are today’s alternatives that have come up again with the need to extend the life of products or materials in order to curb the environmental impact. It implies thinking back for durable product design and being aware that in the culture of consumerism the media product life cycle is very short (disposable) and impacts on global warming.

**Pre-recycling steps**

In an environmental culture, plastic can be recycled mechanically or chemically (Fig. 1). Transformation depends on the quality of recycled plastic required, and this also depends on the requirements for integrating the remanufacturing of a product in use or a new product based on design requirements.

The pre-recycling steps require energy and the use of volatile solvents, but are crucial to separating and cleaning the appropriate particle size to be used in the chemical recycling or mechanical process. Based on recent studies, it is estimated that when recycling plastic by separating the mixture of PET and HDPE plastics that have very different densities using an infra-red detector (NIR) and manual separation, then applying a series of treatments (pre-washing, separation by X-ray and metal detectors, grinding, filtration, washing, flotation, drying and sieving to finally get fine granules or flakes of recycled polymers), the power consumption of all these operations is 6828 MJ/ton, compared with using virgin plastic which consumes 72,573 MJ/ton, thus energy saving is 91.4%, and the savings impact on the environment is 1.12 t CO2 per tonne of plastic recycling [8].

<table>
<thead>
<tr>
<th>Process</th>
<th>Sub-process</th>
<th>Method</th>
<th>Sub-method</th>
<th>Separated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet shaking</td>
<td>Liquid</td>
<td>Vibration</td>
<td>PET, PVC-PS</td>
<td>[9, 10, 34]</td>
</tr>
<tr>
<td>Gravity</td>
<td>Liquid</td>
<td>Water</td>
<td>HDPE-PP, PET-PVC-PS-ABS</td>
<td>[12, 23, 38]</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Liquid</td>
<td>50% wt ethanol</td>
<td>PP, HDPE</td>
<td>[13]</td>
</tr>
<tr>
<td>Density</td>
<td>Liquid</td>
<td>Water-30% wt CaCl$_2$</td>
<td>PS-ABS, PET-PVC</td>
<td>[13, 15, 20]</td>
</tr>
<tr>
<td>Pre-recycling</td>
<td></td>
<td>Wetting through adsorption</td>
<td>HDPE, PET, PVC, PMMA</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aluminium sulfate</td>
<td>PET, POM, PVC</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Liquid-vapour surface</td>
<td>ABS, PC, PET, HDPE</td>
<td>[16, 13, 25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>tension control</td>
<td>Calcium lignosulfonate</td>
<td>[17, 21]</td>
</tr>
<tr>
<td>Mineral</td>
<td>Electromagnetic feeder</td>
<td>Hot water, Vibrating screen, Bank of flotation cell</td>
<td>NaOH-Detergent, Calignosulfo-Hostaphat</td>
<td>PET, PVC</td>
</tr>
<tr>
<td>processing</td>
<td>Fluidized bed technology</td>
<td>Vertical column Water fluid pipeline</td>
<td>TPU, PVC, PBT, PET</td>
<td>[19, 30]</td>
</tr>
<tr>
<td>Electric</td>
<td>Roll-type corona</td>
<td>Electrostatic separator</td>
<td>Waste printed circuit board (PCB)</td>
<td>No conductor plastics</td>
</tr>
<tr>
<td></td>
<td>Magnetic field</td>
<td>Discharging current of a capacitor</td>
<td>Separating metallic particles from metal-plastic mixtures</td>
<td>Plastic mixtures, metallic particles</td>
</tr>
<tr>
<td></td>
<td>Plasma</td>
<td>Oxygen radicals</td>
<td>Input power of 250W to 400W, a pulse frequency of 2kHz to 12kHz</td>
<td>Carbon fiber composites, PS, PP</td>
</tr>
<tr>
<td>Chemical</td>
<td>Ozonation</td>
<td></td>
<td>PVC</td>
<td>[23, 24]</td>
</tr>
<tr>
<td>methods</td>
<td>Methyl cellulose (MC)</td>
<td>Chemical factors, Gravity factors</td>
<td>ABS and PS, PET, PMMA and PC, POM and PVC</td>
<td>[22]</td>
</tr>
</tbody>
</table>
Separation: To recycle plastics with very similar densities, the separation processes are not simple. These plastics are found in ELV (End-of-Life of Vehicles) and WEEE (Waste Electrical and Electronic Equipment). Many articles have been published on methods of separating plastics of similar density from the most classic, such as floating plastic with water, to remove waste from MSW (Municipal Solid Waste), as well as those listed in Table 1.

Detecting and sorting: different techniques exist: Electromagnetic methods (Near infrared NIR, High resolution imaging X-rays [only separation of PVC from PET] [38], Fluorescent tracer in Ultra violet spectroscopy [inadequacy in the conveyor system at high speeds] [39, 40, 41], the magnetic tracer system [quantities of the order of the percent could engender homogenisation problems and affect the mechanical properties of the polymer] [42, 43], XRF (X-ray fluorescence) spectrometry detection of rare earth oxides, used as tracers, blue light absorption [of dark automotive plastic parts] [39, 41], Waste pharmaceutical blister packages; cryo- or electrostatic separation, and combined processes [44, 45].

Most existing methods have an actual separation rate of 80 to 90%, thus affecting the appearance quality of the final product or finished plastic that has been necessary after separation through another process called chemical recycling.

Chemical recycling. The solubility of plastic has made it possible to develop chemical methods to purify and improve their quality through polar and non-polar solvents (xylene, hexane) and achieve their reprecipitation. Structural modification of the polymer chains by gamma irradiation attack or electron irradiation improves the mechanical properties of plastics making them equal to or superior to virgin resin [61-65]. Supercritical fluids (water, ethylene glycol, alcohols) are also a solution for thermoset solvents (using 200-400°C temperature range and pressures from 20 to 30 MPa). By polymerizing the monomers again, we obtain a high purity polymer like a virgin polymer. Most researchers focus their efforts on achieving an efficient method to produce polymers of good quality, but the investment aspect of energy and environmental issues (CO2 emissions) are mentioned only briefly. Figure 1 shows some of the main techniques for chemical recycling.

Mechanical recycling. The processes widely used industrially for thermoplastics such as extrusion and injection molding consider that the humidity control of the polymer and the compatibility between them achieve an acceptable plastic product. The purity of recycled plastics derived from mechanical recycling is not appropriate as it does not give an acceptable appearance or texture similar to a product with virgin polymers. This is largely due to the incompatibility between plastics that causes problems in the rheology of extrusion or injection. At polymer-polymer interfaces, the resulting mechanical property is lower than those required by the designer. Some processing techniques for thermosetting plastics are shown in Figure 1, in which the monomers obtained from chemical recycling are used for fibers with plates. Mecanic apply techniques such as Solid State Shear Pulverization [66-76]. It remains incompatibility due to dust at nanometric levels. This technique needs to be further developed for quaternary and quinary systems of incompatible plastics. This would eliminate some stages of pre-recycling, especially filtration and flotation.

Culture of recycling or remanufacturing. Waste management is a contributor to global warming through CO2 generation. Indeed, many countries are still burning these dusts as valorization (Municipal Solid Waste (MSW), Waste Electrical and Electronic Equipment (WEEE) and recycling of End-of-Life Vehicles (ELV)).

An effective way of reducing these emissions is to prolong product shelf life through a more robust design; this is one goal of eco-design. Another way
is to develop re-use or remanufacturing solutions to spare parts and adapt them in new products. This means designing products that can be updated independently of technical technology and depending on their history and causes of failure (fatigue, wear, corrosion, creep). It creates a cycle of continuous product improvement and an increase in the cycle product life. A last possibility for the reduction of CO2 is the development of better end of life valorization, such as recycling possibilities for polymer products.

Some countries have already structured their waste pipelines, pushed by the WEEE or ELV regulations or due to a high national level of sustainable requirements. Some others have no specific structures (collecting or recycling) and have to develop and promote all the alternatives for industrial and collective scales.

3. Global Analysis of energy consumption and CO2 emissions by anthropogenic activity

The main sources of CO2 emissions from anthropogenic activities considered in this work are those from packaging and packaging intended for the commercial consumption sector, the manufacture of electrical, electronic equipment and manufacturing of motor vehicles. All these sectors contribute significantly to generating considerable emissions from raw material extraction, processing and energy required, use and final destination at the end of its life cycle, becoming trash is classified Municipal Solid Waste (MSW), Waste Electrical and Electronic Equipment (WEEE) and recycling of End-of-Life Vehicles (ELV).

**Automotive figures and polymer contribution**

51,971,328 units of cars are produced annually worldwide, with an average weight of 1384 kg. The average lifecycle is 14 years [48, 47]. On average, each unit consumes 5.1 liters of gasoline per day and each liter of gasoline combustion emits 2.3 kg of CO2 into the atmosphere. In addition, the energy used to produce a gallon of gasoline is 18.3 MJ [48]. Considering that consumed by MJ emitted 0.019 kg of CO2 [49], the result is a total power consumption of 59.8 PJ/year, and 1.4 Gt CO2/year.

The cost of manufacturing a car is around 20 to 30% of the sale price to final consumers and is estimated at 2040€; considering the average price of gasoline globally in the first quarter of 2011 was 1.35€ [50] the resulting expenditure was 112 G€/year (112 billion €).

Of 1.4 Gt CO2/year emitted into the atmosphere, 13% was due to automobile manufacturing, 50% to the production of gasoline and 37% to the combustion of gasoline in the engine. This means that before customers buy and use their car, 50% of CO2 has already been produced due to the manufacture of gasoline. Figure 1 summarizes quantity, energy, CO2 and cost figures for the different types of waste. Figure 2 shows the radar chart type of the relationship between quantity, energy and CO2 emissions. Vehicle end-of-life profile is indicated by a thick line, and is compared with the other two types of waste. The calculation is described below.

**Figure 1.** Radar graph representing environmental, economic and energy automotive, electronics and municipal waste

Plastics accounted for 6% of the total ELV power consumption with 13% (8.1 PJ/year) and 61%
CO2 (0.86 Gt CO2/year). This indicates that more than half of the CO2 emitted for car manufacture comes from the manufacture of plastics.

The manufacture of electronic devices has a strong impact on consumers, especially in the growth of mobile phones and notebooks (laptops), with an estimated 0.16 Gt of electronics produced and in use annually [51]. According to Liqiu Deng et al. [52] in their study of laptops, the energy required per kilogram of production is 1185 MJ/kg, 80 kg issuing CO2/kg for manufacturing electronics, and energy consumed already in use is 574 MJ/kg and 51 kg of electronic CO2/kg with an average life of 3 years.

**Figure 2.** Radar Graph of plastics only on their environmental CO2, energy and costs

**Electronic devices figures and polymer contribution**

Assuming that the average cost of laptops is 500€/unit (year 2011) with an investment cost per unit of 78%, the energy consumption of a laptop is estimated between 190 to 230 kW, equivalent to 0.2312€/day. From the above estimates of global energy consumption 73,486 PJ/year, 5.5 Gt CO2/year, and spending of 8875 G€/year (8 billion euro), of which 61% is invested in the manufacture of electronics and the rest in the payment of electricity by the consumer.

Of the total emissions of 5.5 Gt CO2/year, 60% occur in manufacturing and 40% in the use of electronics, considering that the electricity comes from fossil fuels. Figure 1 shows graphically the four aspects of electronic equipment (WEEE).

Plastics represent 36% of the total weight of WEEE waste, consumes energy but 46% (33 893 PJ/year) and 26% CO2 (1.46 Gt CO2/year), see Figure 2.

**Municipal waste figures and polymer contribution**

Municipal solid waste generates approximately 3.1 Gt/year worldwide, resulting in a major urban problem in the world, because it represents a source of infection with about 0.11 Gt/year of food. Conservative estimates by various authors suggest that each human being contributes 454 kg of municipal waste per year [53-58], energy consumption and CO2 emissions by treating these products: the solid part needs 47 MJ/kg and emits 0.9 kg CO2/kg, the glass 9.4 MJ/kg and 0.18 kg CO2/kg, the plastic 68.7 MJ/kg and 1.3 kg CO2/kg and the metal 26 MJ/kg and 0.49 kg CO2/kg [49].

Conservative estimates result in a power consumption of 71.8 PJ/year, 1.3 Gt CO2/year and [51] 702 G€/year (702 billion euros), these are represented in Figure 1.

**Figure 3.** Radar Graph of the main plastics from MSW, WEEE and ELV in Gt/year

Plastics make up 10% by weight of total MSW, consumed energy but 76% (55 PJ/year) and 64% CO2 (0.83 Gt CO2/year), this indicates the strong
ecological impact of plastic MSW, see Figure 2.

Figure 2 shows that total CO2 emissions from ELV plastics, MSW and WEEE are 3,150,000,000 tons (three billion tons), the amount generated by weight (tons) is very different from CO2 emissions, as plastics manufactured for WEEE are much lower than that produced by MSW and more than that by EVL, this is shown in the logarithmic radar graph in Figure 3.

Figure 3 shows the tons generated annually and highlights the amount of PUR used in automobiles, followed by PP, PE, PVC and PS values, which are much higher than those produced by MSW and WEEE. MSW is dominated by PE and PVC, followed by PET and ABS. The WEEE is predominantly PP, PS and PC. It can be seen in Figure 3 that the PP, PS and PVC are in MSW, WEEE and ELV, which gives an opportunity to explore different plastics that come from industry and can be used in any of the other sectors.

4. Analysis of some chemical recycling processes from the standpoint of energy and environment

As there is not enough real data to propose chemical recycling processes which can give a favorable result in the production of plastic, we present a thermodynamic analysis of energy consumption and CO2 emissions of this process. The results help identify areas of opportunity for improvement and optimizing the process to reduce effort in more CO2 emissions by modifying or adapting existing technology. Consequently, recycling processes are themselves consistent with the clean process environment.

Dissolution – reprecipitation process for thermoplastic HDPE

Figure 4 analyzes the dissolution-reprecipitation process [77]. It involves dissolving a polymer (HDPE) in xylene heated to 150°C, then cooled to 25°C. With the addition of a large amount of hexane (compared with xylene) and heated to 80°C, this initiates the reprecipitation of the polymer that is cooled naturally to 25°C.

Figure 4 (a) shows a radar graph logarithmic of 1kg of plastic obtained. After the process, 0.985 kg is recovered. The solvents are evaporated directly into the atmosphere. Figure 4 (a) shows the values of energy input (MJ), CO2 emissions and production costs in euros (investment cost per plant is not considered in this analysis).

Propositions (b) and (c) are evolutions from the initial device and show process improvements.

Figure 4 (b) amending the process in the first phase, cooling the xylene from 150°C to 60°C (below the temperature of evaporation of hexane) followed by heating to 80°C. In addition, a distillation tower is installed to induce draft and a condenser to recover the solvents. This leads to a decrease in the energy expended on CO2 emissions by half and also reduces manufacturing cost.

Figure 4 (c) is another evolution. The heat source comes from a solar heater. The manufacturing cost of this recycling process is drastically lower this recycling process.

Irradiated base process for thermoplastics

Figure 5 shows a logarithmic radar chart for 1 kg of plastic. The recycling process is based on irradiation solution technology, and compares two sources. The first, Figure 5 (a) uses cobalt-60 nuclear power and gamma radiations [61], and Figure 5 (b) profile is for electron irradiation [61-65] (electrostatically accelerated by generating enough energy to radiate electrons). This radiation can modify the polymer chains of the plastics, thus modifying their properties. Gamma irradiation (a) is a clean process without generation of CO2 and a much lower energy investment cost than with electron irradiation (b).

But this analysis does not take into account the nuclear waste impact. Thus quick conclusions should be avoided and a global analysis must be done to effectively compare the different solutions. Again, huge differences appear between different countries, regarding nuclear waste management.
Figure 4. Logarithm radar graph for improving the dissolution-reprecipitation process.

Figure 5. Analysis of recycled (a) gamma irradiation and (b) electron irradiation
Thermosetting recycling using ethanol

Figure 6 analyzes the depolymerization of carbon-epoxy composites. The thermosetting plastic (epoxy resin 1kg) is extracted with methanol as a solvent. It needs fluid under supercritical behavior [60].

There is a huge need of energy (impact calculation based on nuclear plants) for high pressure and fluid temperatures (275°C and 28 MPa) in order to separate the epoxy matrix from the carbon-reinforced fibers. Alternatives using water solvent are under development and guarantee good mechanical properties of the recycled carbon fibers [59].

PC recycling with solvolysis

Figure 7 shows PC recycling (1 kg polycarbonate) in a reactor at 250°C and 21MPa, using water as a solvent and catalyst Ca2CO3. The depolymerization process recovers 0.69 kg of phenol, bisphenol A, and p-isopropenylphenol, which have a profitable value in the market [78, 79]. The energy impact calculation is based on a fuel oil plant.

5. Conclusions

The product life cycle is closely linked to the recycling processes and especially to the possibility of remanufacturing the product; this can be achieved by detection of product failures and ongoing feedback on product design. The purpose of either mechanical or chemical recycling is based on the needs identified in remanufacturing. The quality of the plastic transformation process is subject to continuous improvements being sought, leading to product improvements. Plastic product designers must consider design platforms where they can keep the product with a much longer life cycle and where parts of the product or spare parts may be remanufactured. This would reduce CO2 emissions dramatically.

Plastics recycling processes should be valued currently from an energy standpoint (MJ), ecological emission (CO2) and profitability (here in €). This requires support from thermodynamics calculations. We observed that recycling processes can be subjected to this thermodynamic analysis and be capable of being improved by the inclusion of clean technology like solar energy; this leads us to develop clean recycling techniques where the final objective is to reduce CO2 emissions.

References

[4] R. Wassmann, H. Pathak, Introducing greenhouse gas mitigation as a development objective in rice-


[50] petrolnews.net/noticia.php?id=7d13938ee3aebee8569e9badfa349c8&r=15896.


[54] M. E. Kaseva, S. E. Mbuligwe, G. Kassenga, Recycling inorganic domestic solid wastes: results from a pilot study in Dar es Salaam City,


