

Ex-ante life cycle engineering

**Application to nanotechnology and white
biotechnology**

Ex-ante levenscyclus engineering

Toepassing op nanotechnologie en witte biotechnologie

(met een samenvatting in het Nederlands)

Proefschrift

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Contents

List of abbreviations	v
Executive summary.....	xi
1 Introduction.....	1
1.1 Background	1
1.2 Technology assessment	6
1.3 Life cycle engineering – principles and outline	8
1.3.1 Life cycle assessment.....	10
1.3.2 Life cycle costing.....	12
1.4 Focus of this thesis	13
References.....	17
2 Environmental and cost assessment of a polypropylene nanocomposite	21
Abstract.....	21
2.1 Introduction.....	22
2.2 Environmental assessment: Life cycle assessment.....	23
2.2.1 LCA fundamentals	23
2.2.2 Goal definition and scoping	24
2.2.3 Inventory analysis	30
2.2.4 Results: Life cycle impact assessment.....	37
2.2.5 Discussion and conclusions: Life cycle interpretation.....	40
2.3 Economic assessment: Life cycle costing	44
2.3.1 Methodology	44
2.3.2 Goal and scope definition	44
2.3.3 Cost calculations	44
2.3.4 Interpretation of the results	46
2.4 Conclusions	47
Acknowledgements	48
References.....	49
3 Influence of using nanoobjects as filler on functionality based energy use of nanocomposites	53
Abstract.....	53
3.1 Introduction.....	54
3.2 Methodology	57
3.2.1 Approach.....	57
3.2.2 Environmental assessment of nanoobjects.....	58

3.3	Results	64
3.4	Discussion	74
3.4.1	Analysis of factors influencing mechanical properties.....	74
3.4.2	Extrusion.....	78
3.4.3	Uncertainties.....	80
3.5	Conclusions	84
	Acknowledgements	86
	References	87
4	Preliminary assessment of the risks related to the waste management of polymer nanocomposites.....	93
	Abstract	93
4.1	Introduction	94
4.2	Approach	95
4.3	Toxicity of free nanoobjects	96
4.4	Analysis of the MSWI process related to the fate of nanoobjects	98
4.4.1	The waste incineration process.....	98
4.4.2	Processes that affect the potential release of free nanoobjects.....	99
4.5	Preliminary risk assessment for a subset of nanoobjects	108
4.6	Discussion	115
4.7	Conclusions	116
	Acknowledgements	117
	References	118
5	Ex-ante environmental and economic evaluation of polymer photovoltaics.	123
	Abstract	123
5.1	Introduction	124
5.2	Environmental assessment	125
5.2.1	LCA fundamentals.....	125
5.2.2	Goal definition and scoping.....	125
5.2.3	Inventory analysis.....	127
5.2.4	Results: Impact assessment.....	142
5.2.5	Life cycle interpretation: Discussion and conclusions.....	145
5.3	Life cycle costing	149
5.3.1	Methodology.....	149
5.3.2	Goal and scope definition.....	149
5.3.3	Cost calculations.....	150
5.3.4	Interpretation of the results.....	151
5.4	Discussion	152
5.4.1	Uncertainties regarding costs of module assembly.....	152
5.4.2	Assuming higher efficiencies.....	153
5.4.3	Perspectives.....	154

5.5 Conclusions	154
Acknowledgements	156
References	157
6 Life cycle risks for human health: a comparison of bio-based versus petroleum-based production of 5 bulk organic chemicals	165
Abstract	165
6.1 Introduction	166
6.2 Methodology	167
6.2.1 External risks due to regular release of emissions	168
6.2.2 External risks due to technological disasters	170
6.2.3 Accidents.....	170
6.2.4 Work-related illnesses.....	171
6.2.5 Risk indicator matrix.....	172
6.3 Results	173
6.4 Uncertainties	180
6.4.1 Ranges of input data.....	180
6.4.2 Uncertainty analysis for accidents and illnesses.....	180
6.4.3 Coverage of emissions by EPS 2000	181
6.4.4 Plausibility check by comparison with other literature data.....	182
6.5 Conclusions	183
Acknowledgements	184
References	185
7 Conclusions	189
7.1 Improvements and extensions to the existing LCE methodology	189
7.2 Nanotechnology	192
7.3 White biotechnology	194
Samenvatting in het Nederlands	197
Dankwoord	205
About the author	209

List of abbreviations

AC	Alternating current
APME	Association of Plastics Manufacturers Europe – currently known as PlasticsEurope
BGS	Sugar cane bagasse
BMS	Bayer Material Science
BOS	Balance of system
C ₆₀	Buckminster fullerene
CB	Carbon black
CENTREL	Organization for the Electricity Transmission System Operators of Hungary, Czech Republic, Poland and Slovak Republic
CFC-11-eq	Trichlorofluoromethane equivalents
CFCs	Chlorofluorocarbons
CIS	Copper Indium Selenide
CML	Centrum voor Milieukunde Leiden / Institute of environmental sciences Leiden
CO ₂ -eq	Carbon dioxide equivalents
Conv	Conventional
CTA	Constructive technology assessment
DC	Direct current
DCS	Dye-sensitized cells
DDT	Dichlorodiphenyltrichloroethane
DfE	Design for the environment
DI	Deionized
DNA	Desoxyribonucleic acid
ECA	European Chemicals Agency
EDOT	3,4-ethylene dioxythiophene
Emiss.	Emissions
Ep	Epoxy
EPA	Environmental Protection Agency
EPDM	Sulfonated ethylene-propylene-norbonene terpolymer
EPS	Environmental Priorities Strategies
Eq.	Equation
ESP	Electrostatic precipitator
EVA	Ethylvinylacetate
Fte	Fulltime equivalent
FU/f.u.	Functional unit

GF	Glass fibre
GMO	Genetically modified microorganisms and plants
GWP ₁₀₀	Global Warming Potential in the next 100 years
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HEPA	High efficiency particulate air
HHV	Higher heating value
HiPco	High-pressure carbon monoxide
ICT	Information and communication technology
IP	Integrated production
IPA	Isopropyl alcohol
IPCC	Intergovernmental Panel on Climate Change
IPF	Institut für Polymerforschung / Institute for Polymer Research
ISO	International Standards Organization
ITO	Indium tin oxide
LCA	Life cycle assessment
LCC	Life cycle costing
LCE	Life cycle engineering
LCI	Life cycle inventory
LDPE	Low-density polyethylene
LED	Light-emitting diode
LiF	Lithium fluoride
LLDPE	Linear low-density polyethylene
mc	Multicrystalline
MI	Material index
MMT	Montmorillonite
MSWI	Municipal solid waste incineration
MWNT	Multiwalled carbon nanotubes
Nanocomp.	Nanocomposite
NORDEL	Organization for the Nordic Electricity Transmission System Operators
NO _x	Nitrogen oxides
NR	Natural rubber
NREU	Non-renewable energy use
ODA	Octadecylamine
OTR	Oxygen transmission rate
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PC	Polycarbonate
PCB	Polychlorinated biphenyls
PCBM	[6,6]-Phenyl C ₆₁ -butyric acid methylester

PCL	Poly(ϵ -caprolactone)
PE	Polyethylene
PEDOT	Poly(3,4-ethylene dioxythiophene)
PET	Polyethylene terephthalate
PHA	Polyhydroxyalkanoates
PHB	Poly(hydroxybutyrate)
PLA	Poly(lactic acid)
PM	Particulate matter
PMMA	Poly(methyl methacrylate)
PO ₄ ³⁻ -eq	Phosphate equivalents
POSS	Polyhedral oligomeric silsesquioxane
PP	Polypropylene
PP-g-MA	Maleic anhydride-grafted polypropylene
PS	Polystyrene
PSS	Poly(styrenesulfonate)
PTT	Poly(trimethylene terephthalate)
PU	Polyurethane
PV	Photovoltaic
PVC	Polyvinylchloride
PVF	Polyvinylfluoride
R&D	Research and Development
REACH	Registration, Evaluation, Authorization and restriction of CHemicals
Sb-eq	Antimony equivalents
SETAC	Society for Environmental Toxicity and Chemistry
SO ₂	Sulphur dioxide
SO ₂ -eq	Sulphur dioxide equivalents
SWNT	Singlewalled carbon nanotubes
TBT	Tributyltin
TPES	Total primary energy supply
TPS	Thermoplastic starch
UCTE	Union for the Co-ordination of Transmission of Electricity
UFP	Ultrafine particles
UV	Ultraviolet
VAT	Value added tax
VOC	Volatile organic compounds
Waste mmt	Waste management
W _p	Watt-peak
XLDPE	Cross-linked low-density polyethylene
YOLL	Years of life lost

Units

K	Kelvin
°C	degree Celcius
nm	nanometre
µm	micrometre
cm	centimetre
mm	millimetre
dm	decimetre
m	metre
km	kilometre
tkm	tonnekilometre
cm ²	square centimetre
dm ²	square decimetre
m ²	square metre
km ²	square kilometre
ha	hectare
cm ³	cubic centimetre
dm ³	cubic decimetre
m ³	cubic metre
l	litre
µg	microgramme
mg	milligramme
g	gramme
kg	kilogramme
t	1) tonne (metric) 2) 'thickness' on p 27
E	Young modulus
σ _r	Tensile strength
ρ	Density

kJ	kilojoule
MJ	megajoule
MJ _e	megajoule electricity
GJ	gigajoule
GJ _e	gigajoule electricity
GJ _p	gigajoule primary energy
TJ	terajoule
W	Watt
kWh	kilowatt-hour
MPa	megapascal
GPa	gigapascal
yr	year

Executive summary

Scientific research and technological innovation have brought major progress to mankind. The inventions that emerged from science provided the basis for the modern society as we know it today. The manufacturing of new advanced materials is at the heart of this era. New technologies are developing continuously, examples being nanotechnology, industrial – or ‘white’- biotechnology, metamaterials, quantum dots, high-temperature superconductivity, programmable matter and self-healing materials. Although new technologies have brought major progress to society, there are also large trade-offs; the scale of human activities is enormous and exceeds the capacity of the environment to cope with the resulting impacts. Large environmental problems are a consequence of this development. Some materials have entered the market that particularly have caused severe problems to humans or the environment. Examples are benzene, asbestos, polychlorinated biphenyls, halocarbons, tributyltin, and dichlorodiphenyltrichloroethane (DDT). In order to evaluate potential harmful effects of technologies and products, they have to be systematically assessed. The analysis and evaluation of consequences, chances and risks of new and established technologies is referred to as ‘technology assessment’. The adverse effects of the materials just mentioned became apparent only after they had already been widely applied. It is therefore crucial that new materials and technologies are evaluated before they have entered the market. For novel technologies, the focus should therefore be ‘ex-ante’ (i.e. future-oriented).

In this thesis we applied ex-ante technology assessment to two emerging technologies: nanotechnology and white biotechnology. These two technologies are considered as very important technologies in chemical manufacturing industry and material science with huge potentials for the future (both are sometimes referred to as technologies causing a ‘revolution’ in science and society). The technology assessment we applied is referred to as ‘life cycle engineering (LCE)’. Life cycle engineering includes the integration of ‘life cycle assessment (LCA)’ and ‘life cycle costing (LCC)’. LCA is a methodology to assess the environmental impacts of a product or technology throughout its life cycle from ‘cradle’ (i.e. from resource extraction), to ‘grave’, (i.e. to the waste stage). LCC is a similar methodology but focuses on economic aspects. Life cycle engineering aims at improving a product’s performance throughout its life cycle.

At this moment, the concept of life cycle engineering is still in an early stage and therefore does not always offer the possibility to fully assess technologies on all relevant

aspects. Especially for ex-ante assessments, there are several issues for which the LCE methodology does not provide sufficient tools for a comprehensive analysis. In this thesis, we therefore try to contribute to the following general research question:

How could the existing methodology of life cycle engineering be improved or extended to allow a more comprehensive ex-ante assessment of new technologies and what problems or uncertainties still need to be solved?

For white biotechnology, it is very important that risks to human health are identified at an early stage. At this moment, existing impact assessment methods for this purpose are insufficient. Although many methods include health effects, they do not address the effect of work-related accidents and/or diseases. This thesis therefore aims at contributing to the development of an improved methodology. The following subquestion is defined:

How can a generic ex-ante assessment of conventional risks be conducted for chemicals over the entire life cycle (i.e. cradle-to-factory gate plus waste stage)?

At the level of the inventory data, the LCE methodology could be improved as well: To compare a new product or technology that is still in the laboratory stage with a conventional product or technology is challenging, because life cycle data for the future, large scale application of the new product/technology are often not available (such as for nanocomposites or polymer photovoltaics). An attempt is made in this thesis to contribute to this issue. The following subquestion is addressed in this thesis:

How can inventory data be estimated that represent large scale industrial practice for products or technologies that are still in the laboratory stage?

Given the importance of nanotechnology and white biotechnology as emerging technologies there is a need for the early assessment of chances and risks of these technologies. Assessments covering all aspects of these technologies are not possible in a single thesis, but the ex-ante evaluation of a subset of technologies is an achievable task. In this thesis, the following research questions are answered:

What are the chances and risks of nanotechnology from an environmental and economic perspective, focusing on polymer nanocomposites and polymer photovoltaics?

What are the chances and risks of white biotechnology, taking into account risks to human health and focusing on the bio-based production of polytrimethylene terephthalate (PTT), polyhydroxyalkanoates (PHA) and ethanol?

The research questions defined above are answered in Chapter 2-6.

Chapter 2 studies the use of a polypropylene (PP)/layered silicate nanocomposite as packaging film, agricultural film, and automotive panels. The goal of the study is to evaluate environmental impacts and costs throughout the life cycle of PP-nanocomposite products compared to products manufactured from conventional materials. The conventional (benchmark) materials studied are pure polypropylene as packaging film, pure polyethylene as agricultural film, and glass fiber-reinforced polypropylene as automotive panels. In all three cases, the use of the PP nanocomposite allows to reduce the amount of material used, while ensuring the same functionality.

It might seem logical that a product's impact on the environment will decrease when less material is used. The production and incorporation of nanoparticles, however, may cause additional impacts. We found clear environmental benefits throughout the entire life cycle when the PP nanocomposite is used for the manufacture of agricultural film, while they were generally low to very low for packaging film and automotive panels. We noted some cost benefits when the nanocomposite is used in the production of agricultural film and automotive panels. If the price of nanoclay is below €5000/tonne, then the cost of nanocomposite packaging film is also lower compared to the conventionally produced product.

In this chapter, the use of Ashby's material indices is introduced to estimate material use of a novel material compared to a conventional material for the same function. The Ashby indices appeared to be a useful tool for the ex-ante assessment of material requirements of novel materials. Being a generic methodology, it provides a first indication of the influence of material properties (such as Young's modulus, tensile strength and density) on the material requirements and, as such, can be used when data from industrial practice are not available.

In Chapter 3 the potential benefits of reinforcing polymer matrices with nanoobjects for structural applications are investigated by looking at both the mechanical properties and environmental impacts. For determining the mechanical properties we applied the material indices defined by Ashby for stiffness and strength. For the calculation of environmental impacts we applied the life cycle assessment methodology, focusing on non-renewable energy use (NREU). NREU has shown to be a good indicator also for other environmental impacts. We then divided the NREU by the appropriate Ashby index to obtain the 'functionality based NREU'.

We studied twenty-three different nanocomposites, based on thermoplastic and thermosetting polymer matrices and organophilic montmorillonite, silica, carbon nanotubes (singlewalled and multiwalled) and calcium carbonate as filler. For seventeen of these, we saw a decrease of the functionality based NREU with increasing filler content. We draw the conclusion that the use of nanoobjects as filler can have benefits from both an environmental point of view and with respect to mechanical properties.

If nanotechnology proves to be successful for bulk applications, large quantities of nanocomposites are likely to end up in municipal solid waste incineration (MSWI) plants. Various studies indicate that nanoobjects might be harmful to human health and the environment. At this moment there is no evidence that all nanoobjects are safely removed from the off-gas when incinerating nanocomposites in MSWI plants. Chapter 4 presents a preliminary assessment of the fate of nanoobjects during waste incineration and the ability of MSWI plants to remove them. It appears that many primary and secondary nanoobjects arise from the incineration of nanocomposites and removal seems insufficient for particles that are smaller than 100 nm. For the nanoobjects studied in this research, risks occur for aluminium oxide, calcium carbonate, magnesium hydroxide, POSS, silica, titanium oxide, zinc oxide, zirconia, mica, montmorillonite, talc, cobalt, gold, silver, carbon black and fullerenes. Since this conclusion is based on a desktop study without accompanying experiments, further research is required to reveal which nanoobjects will actually be emitted to the environment and to determine their toxicity to human health.

The use of polymer materials for photovoltaic (PV) applications is expected to have several advantages over current crystalline silicon technology. The advantages include easy processing of the materials and possible economic benefits. In Chapter 5, we perform an environmental and economic assessment of polymer-based thin film modules with a glass substrate and modules with a flexible substrate and we compare our results with literature data for multicrystalline (mc-) silicon photovoltaics and other types of PV. Because the lifetime of polymer photovoltaics is at present much lower compared to mc-silicon photovoltaics, we first compared the PV cells per watt-peak and next determined the minimum required lifetime of polymer PV to arrive at the same environmental impacts as mc-silicon PV.

We found that per watt-peak of output power, the environmental impacts compared to mc-silicon are 20-60% lower for polymer PV systems with glass substrate and 80-95% lower for polymer PV with PET as substrate (flexible modules). Also in comparison with thin film CuInSe and thin film silicon, the impacts of polymer modules, per watt-peak, appeared to be lower. The minimum required lifetime to break even with mc-silicon for

polymer PV with a glass substrate is roughly 10-20 years and for flexible modules it is roughly 1-5 years.

The costs per watt-peak of polymer PV modules with glass substrate are approximately 20% higher compared to mc-silicon photovoltaics. However, taking into account uncertainties, this might be an overestimation. For flexible modules, no cost data were available. If the efficiency and lifetime of polymer PV modules increases, both glass-based and flexible polymer PV could become an environmentally friendly and cheap alternative to mc-silicon PV.

Chapter 6 describes the development and application of a generic approach to the comparative assessment of risks related to the production of organic chemicals by white biotechnology versus petrochemical processes. White biotechnology typically uses bio-based feedstocks instead of the fossil raw materials used in the petrochemical sector. The purpose of this study was to investigate whether the production of chemicals by means of white biotechnology causes lower conventional risks than their production by petrochemical processes. Conventional risks are the risks of well-established processes, such as manufacturing, waste processing and transport, and exclude the risks related to genetically modified microorganisms and plants. Our approach combines classical risk assessment methods (largely based on toxicology), as developed by the Life Cycle Assessment (LCA) community, with statistics on technological disasters, accidents, and work-related illnesses. Moreover, it covers the *total process chain* for both bio-based and petrochemical products *from cradle to grave*.

The approach was applied to five products: the plastics polytrimethylene terephthalate (PTT), polyhydroxyalkanoates (PHA), polyethylene terephthalate (PET) and polyethylene (PE) and to ethanol. For PTT and ethanol, bio-based production was compared to petrochemical production. PHA, a bio-based chemical, was compared to PET and PE, both petrochemicals. Our results show that the conventional risks related to the white biotechnology products studied are lower than those of the petrochemical products. However, considering the uncertainties with respect to the ranges of input data, the (incomplete) coverage of emissions by the Environmental Priority Strategies (EPS) 2000 method, and the uncertainties of the assumptions made in this study (i.e., large to very large), the differences in results between bio-based and petrochemical products fall into the uncertainty range. For this reason, future research is necessary to decrease the uncertainties before the conclusion can be drawn that the conventional risks of biotechnologically produced chemicals are lower than those of fossil fuel-derived chemicals.

In this thesis, the chances and risks of nanotechnology and white biotechnology have been studied ex-ante. This thesis has also contributed to an improvement and extension of

the existing methodology of life cycle engineering, allowing a more comprehensive ex-ante assessment of nanotechnology and white biotechnology. The study yielded the following conclusions regarding methodological issues:

- For new technologies that are not yet on the market, it is a challenge to extrapolate laboratory-scale data to an estimate representing industrial practice. For the cases studied this was possible by using laboratory inventory data on material use, energy use and required processes (such as extrusion, spray drying, chemical vapour deposition etc) in combination with data of large-scale industrial practice. Once a realistic set of material and energy requirements has been established that represents industrial practice, an environmental impact assessment can be performed.
- If two materials (a novel and a conventional one) are used for a structural application, the material requirements will differ for each of the materials, being to the advantage of the material with better material properties. It appeared that the Ashby material indices for stiffness and strength provided a simplified, but useful tool for estimating material requirements of a novel material compared to a conventional one (for applications that are determined by the mechanical properties). The method was successfully applied to nanocomposites.
- In Chapter 6 a new impact assessment approach was developed, i.e. an extension of the expression of risks to human health based on a life cycle perspective. All risks are expressed in 'years of life lost (YOLL)'. The method was successfully applied to the life cycles of PTT, PHA, PET, PE and ethanol and could be applied to other chemicals as well.

In the field of nanotechnology, there are good opportunities for polymer nanocomposites and polymer photovoltaics. For the majority of the nanocomposites studied, it was found that the use of nanoobjects as filler increased the mechanical properties to an extent that possible additional impacts related to the production and incorporation of the nanoobjects (health effects excluded) were compensated for. It is concluded that the use of nanoobjects for reinforcement of nanocomposites can be beneficial from an environmental point of view. Depending on the price of nanoclay, there might also be economic advantages. Risks concern mainly the toxicity of the nanoobjects and their possible release to the environment after waste incineration of nanocomposites. Polymer photovoltaics have the potential to compete with existing photovoltaic technologies both on an environmental and economic basis, but then the lifetime has to be increased drastically. The main challenges in polymer PV technology are to increase both the lifetime and the cells' power generation efficiency.

For white biotechnology, no alarming risks were found. It was found that the risks of all bio-based products studied are lower than those of the petrochemical products. However, the uncertainties are substantial and further research is required to establish the conclusions that now seem in favour of the bio-based products.

Ex-ante analyses have successfully been applied in this thesis to nanotechnology- and white biotechnology-based products. The methodology has been improved and extended. The Ashby method has proven to be a good tool for assessing material requirements of novel materials. Furthermore, it has been shown how data for industrial practice can be estimated from lab data. These contributions concern first steps, however, and leave further room for improvement of the approaches taken. Based on the assessments in this thesis we find promising opportunities for nanotechnology and white biotechnology. According to the analyses performed in this thesis these technologies can contribute to a more sustainable society. However, negative side-effects need to be carefully monitored and suitable measures must be taken to minimize them. In order to strengthen the conclusions and to further improve the methodology on ex-ante assessments, we propose further research. Especially the translation from lab-scale data to a reliable estimate for industrial practice should be studied more extensively. Furthermore, experiments should be conducted to determine the exact fate of nanoobjects in the waste incineration process and their impacts.

CHAPTER 1

Introduction

1.1 Background

Scientific research and technological innovation are considered to be indispensable prerequisites of modern life and civilization. Fields of science like chemistry, physics, engineering and health sciences have contributed to an improvement of the human living standard to a level that had never been known before the industrial age. The industrial age started with the scientific revolution in the sixteenth century. Since then, modern science has evolved, leading to numerous inventions, that provided the basis for the modern society as we know it today. In this society, with the advanced manufacturing of millions of products, the development of advanced materials is at the heart of this era. The use of materials has always characterized the ages in which man has lived and has named them: Stone Age, Bronze Age, Iron Age. Modern age could be named 'the age of advanced materials'. The evolution of material science and its increasing pace are illustrated in Figure 1.1. In the pre-history (>10000 BC, the Stone Age), the most commonly used materials were ceramics and glasses, natural polymers and composites. Naturally occurring gold and silver were available locally. With the development of rudimentary thermo-chemistry, the extraction of, first, copper and bronze, then iron (the Bronze Age, 4000-1000 BC and the Iron Age, 1000 BC-1620 AD) became possible, stimulating enormous advances in technology. The dominance of metals in engineering was enabled by cast iron technology (1620s). And since then the evolution of steels (from 1850 onwards), light alloys (1940s) and special alloys increased the importance of metals in engineering. Since 1960, the relative importance of metals has declined and especially the polymer and composite industries have grown rapidly, as did the ceramics industry, thanks to the growth of production of new high-performance ceramics. [1]

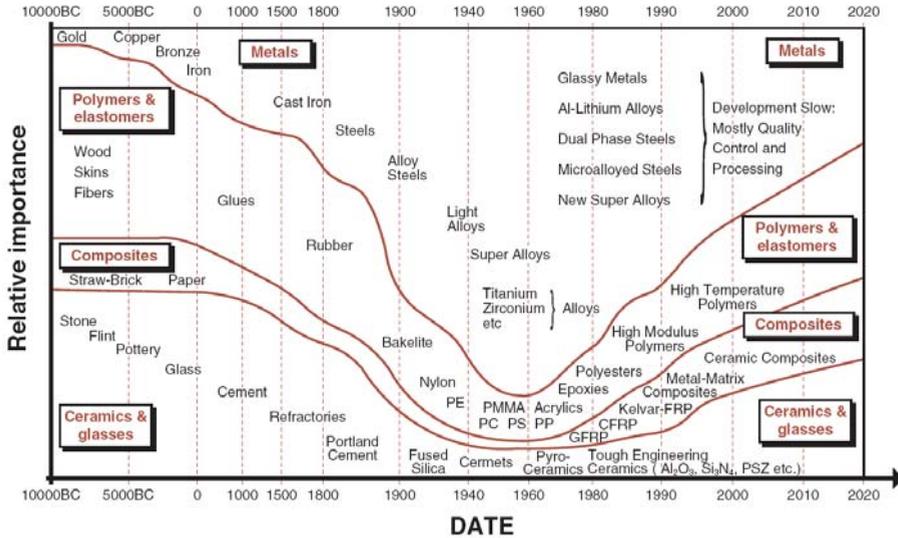


Figure 1.1: The evolution of engineering materials with time [1]. Reproduced with permission of Elsevier.

New technologies in material science are developing continuously. Examples are nanotechnology (i.e. an emerging field of research and development focused on the control of matter on atomic and molecular scale), industrial biotechnology (i.e. the application of biotechnology for industrial purposes, including manufacturing, alternative energy and biomaterials; also referred to as white biotechnology), metamaterials (i.e. artificial materials with properties not readily available in nature), quantum dots (i.e. semiconductors with enhanced properties that could be used in e.g. transistors, solar cells and light-emitting diodes - LEDs), high-temperature superconductivity (i.e. the development of materials that have superconductive properties above 30K), programmable matter (i.e. matter which has the ability to change its physical properties, such as shape, density, moduli, optical properties, etc., in a programmable fashion, based upon user input or autonomous sensing) and self-healing materials (i.e. materials that have the built-in ability to partially repair damage occurring during its service lifetime).

Although the development and large-scale application of new technologies and advanced materials has brought major progress to mankind, it is nearly always accompanied by tradeoffs. The scale of human activities is enormous and exceeds the capacity of the environment to cope with the resulting impacts [2]. The production and use of products, with their associated consumption of materials and energy, is a large contributor to this

problem. Natural resources are being depleted, including fossil energy reserves; emissions resulting from the production of materials and generation of energy contribute to climate change, acidification of soil and water, eutrophication of aquatic habitats, photochemical oxidant formation in air and toxicity to humans, animals and plants. [3] Some materials have caused particularly severe problems to humans or the environment. A report by the European Environment Agency [4] includes the following examples: Benzene, asbestos, polychlorinated biphenyls (PCBs), halocarbons, fossil fuels and tributyltin (TBT).

Benzene has been used as a solvent since 1910 in numerous industries (including leather industry, rubber goods, glue manufacturing, paint, adhesives and coatings), as a starting material in organic synthesis, in petroleum products and as motor fuel additive. It appeared, however, that benzene is very toxic and workers exposed to it developed diseases like leukaemia and aplastic anaemia. [5]

Asbestos is a naturally occurring silicate mineral with long, thin fibrous crystals. Asbestos became increasingly popular among manufacturers and builders in the late 19th century because of its resistance to heat, electrical and chemical damage, sound absorption and tensile strength. After asbestos had been used for some decades, scientific evidence appeared on serious diseases related to exposure to asbestos. Asbestos was proven to cause mesothelioma (asbestos cancer), which is normally fatal within one year. [6]

PCBs are chlorinated organic compounds that were first synthesized in the laboratory in 1881. They have the same basic chemical structure, and similar physical properties as some naturally occurring products, ranging from oily liquids to waxy solids. They were well received in the marketplace as they replaced products that were more flammable, less stable and bulkier. However, workers exposed to PCBs developed a pathological condition named chloracne, a painful disfiguring skin disease. Furthermore, autopsy on some workers that had died after being employed in the chlorinated organic industry revealed severe liver damage. [7]

Halocarbon compounds are chemicals in which one or more carbon atoms are linked by covalent bonds with one or more halogen atoms (fluorine, chlorine, bromine or iodine). Chlorine halocarbons are the most common and are called organochlorides. Common uses for halocarbons have been as solvents, pesticides, refrigerants, fire-resistant oils, ingredients of elastomers, adhesives and sealants, electrically insulating coatings, plasticizers, and plastics. By the 1970s, it was generally accepted by the scientific world that the use of chlorofluorocarbons (CFCs) as refrigerant is the main cause for the

depletion of the stratospheric ozone layer. The ozone layer absorbs 93–99% of the sun's high frequency ultraviolet light, which is potentially damaging to life on earth (e.g. it causes skin cancer in humans). There is an ozone hole over Antarctica from September to December each year, large ozone losses in the Arctic and moderate ozone losses in the middle latitudes of both hemispheres. [8]

The use of fossil fuels (mainly coal and fuel oil) for the generation of power and heating of buildings has resulted in large emissions of sulphur dioxide (SO₂) and nitrogen oxides (NO_x) into the air. This caused a problem commonly known as 'acid rain'; as a result of SO₂ and NO_x in the air, precipitation became more acidic, resulting in severe damage to forests, acidification of rivers and lakes and declining stocks of fish. [9]

TBT is a biocide that was used as paint on vessels and man-made structures at sea to prevent the accumulation of marine fouling communities. The release of TBT into the seawater had a very harmful effect on marine life. In the Arachon Bay in France (an important area for oyster culture), TBT affected the reproduction of oyster leading to the collapse of the shellfish industry in that area. In other areas, a phenomenon called 'imposex' was observed in marine gastropod molluscs; female organisms developed male sexual organs. [10]

Apart from the ones just described there are more examples, such as dichlorodiphenyltrichloroethane (DDT), dioxin and mercury compounds. DDT is one of the most well-known synthetic pesticides. However, DDT has shown to be toxic to a wide range of animals in addition to insects. DDT accumulates in the food chain and as a result is found in organisms in remote parts of the world that had never been exposed to direct use of DDT. Besides, DDT is very toxic to humans. [11, 12] Dioxins occur as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride) and in the bleaching of paper. Also dioxins are very toxic to humans and to animals as they accumulate in fats. [13]. Mercury has been used primarily for the manufacture of industrial chemicals and for electrical and electronic applications. Products containing mercury include: auto parts, batteries, fluorescent bulbs, medical products, thermometers, and thermostats. Apart from that, mercury is released from coal combustion. Mercury and mercury compounds appeared to be extremely toxic to humans. Therefore, most countries have implemented strict regulations concerning mercury. For example, the United States Clean Air Act, passed in 1990, put mercury on a list of toxic pollutants that need to be controlled to the greatest possible extent. [14]

Furthermore, human activities such as transportation, coal combustion, cement manufacturing, metallurgy and waste incineration produce primary aerosol particles, also

named ‘fine dust’ or ‘particulate matter’. Particulate matter receives attention nowadays, because it has shown to exhibit complicated effects on the climate [15]. Besides, effects of inhaling particulate matter have been widely studied in humans and animals and include asthma, lung cancer, cardiovascular issues, and premature death (e.g. [16]). In this respect, large health risks are expected for a new type of ultrafine particles, i.e. nanoobjects that have a size of $< 0.1 \mu\text{m}$ (100 nm). Measures have to be taken to avoid emissions resulting from the emerging field of nanotechnology and possibly also due to the incineration of large amounts of nanocomposites (see Chapter 4).

Figure 1.2 gives an overview of the relationship between the start of industrial production versus the year that effective policy measures started to be implemented to fight adverse effects for some of the materials just discussed. As can be seen from the figure, for substances like PCB and halocarbons, it took almost a century before effective measures were taken. For dioxin it even took more than a century. It should be mentioned, that although first asbestos regulations were set in 1931, it was not until 1998 until a complete ban on the use of asbestos was implemented.

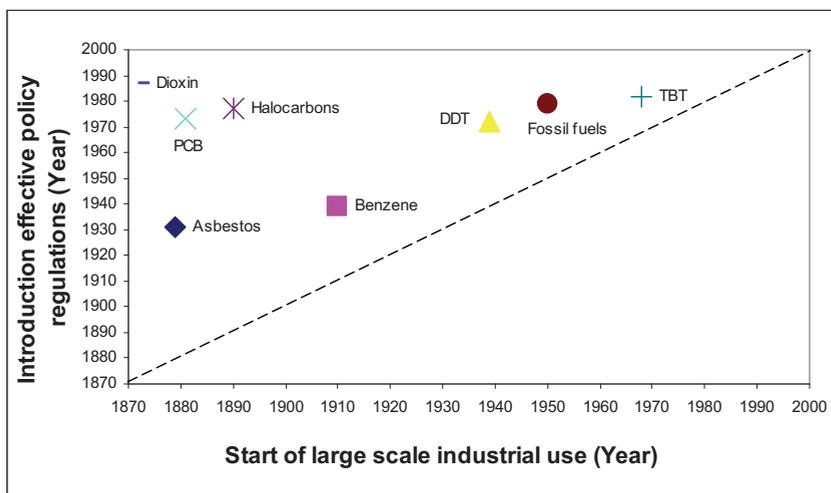


Figure 1.2: Overview of the period between introduction in the market versus the introduction of policy measures related to some hazardous substances.

1.2 Technology assessment

In order to evaluate potential harmful effects of technologies and products, they have to be systematically assessed. 'Technology assessment' aims at analyzing and evaluating the desirable and non-desirable consequences, the chances and the risks, of new technologies as well as established technologies. Technology assessment can assess consequences on a global, regional or local scale and is future-oriented. Technology assessment considers its task as 'an interdisciplinary approach to solving already existing problems and preventing potential damage caused by the uncritical application and the commercialization of new technologies' [17]. Therefore any results of technology assessment studies must be published, and particular consideration must be given to communication with political decision-makers. [17]

Technology assessment has evolved since the mid-1960s through various historical developments in society. Since the beginning of industrialization at the end of the eighteenth century, technology had widely been considered as an inevitable driver of social progress and prosperity. Technology in the first period was mainly connected to economy and production processes. After the second world war, technology played an important role in rebuilding society and a tremendous expansion of the research system in the industrialized world began, leading to an ever increasing offer of technology in all parts of society. In this period, however, also other effects of technology were observed: Society became completely dependent on technology and the penetration of technology into society is irreversible. People also feared the loss of jobs, if technology takes over many functions, previously occupied by men. And, very important, technology started being a major cause of large-scale environmental problems. In the mid-1960s the need for governing technologies was felt throughout society. Not only the pace of technology development, but also how technologies develop should be controlled. Moreover, potential harmful effects of new technologies should be identified in an early stage ('early warning signal'). This led to the concept of technology assessment. Smits and Leyten (1991) define technology assessment as following:

"Technology assessment is a process consisting of analyses of technological developments and their consequences, and debates as a result of these analyses. Technology assessment has the aim to deliver information to stakeholders that helps them in developing strategic policy and that helps them to define topics for further technology assessment research." [18]

It should be noted that the moment the technology assessment takes place is of crucial importance for society and actors involved in the technology. As was seen with the materials listed previously, the adverse effects of these substances became apparent only

after they had already been widely applied. Furthermore, large-scale technologies such as nuclear power plants, high rise tower blocks and the Channel tunnel project faced the problem that early in the development, too little robust data (on benefits, costs, safety implications and so on) were available on which decision makers could base important decisions about whether to invest or not. Knowledge about such impacts became available too late to be of help, since large investments had already been made and some severe negative impacts were experienced. [19]

As a result of this, the policy environment is changing and concepts are being developed to prevent adverse effects rather than having to combat them when new technologies have already widely penetrated into society. There is a need to assess chemicals and technologies before they have entered the market. A type of technology assessment that focuses on the evaluation of new technologies in an early stage of development is 'constructive technology assessment (CTA)'. The focus of CTA is 'ex-ante', i.e. it is performed when the technology is still in the early research stage and the future development and introduction in the market of the technology can still be steered. Important in CTA is the early involvement of all actors and their participation in the technology design and development practices. [20-24]

An example of an initiative where the focus is on 'prevention' of environmental damage is 'Design for the Environment - DfE'. DfE is an initiative of the U.S. Environmental Protection Agency (EPA) and works in partnership with industry, environmental groups, and academia to reduce risk to people and the environment by finding ways to prevent pollution. For more than 15 years, DfE has evaluated human health and environmental concerns associated with traditional and alternative chemicals and processes in a range of industries. These analyses have empowered hundreds of businesses to select safer chemicals and technologies. [25]

A comparable concept is 'Ecodesign'. Ecodesign takes into account the entire life cycle of products and focuses on the improvement of processes which show especially high impact on the environment. The aim is to design more environmentally friendly products. This is in line with the European directive 2009/125/EG by which the European Commission can demand the ecological design of energy related products. [26]

Another regulation which has been implemented to avoid future environmental damage is REACH (Registration, Evaluation, Authorisation and restriction of CHemicals). This European Union Regulation of 18 December 2006 addresses the production and use of chemical substances and their potential impacts on both human health and the environment. REACH requires all companies manufacturing or importing chemical substances into the European Union in quantities of one tonne or more per year to register these substances with a new European Chemicals Agency (ECA) in Helsinki, Finland. Supply of substances to the European market which have not been pre-registered or registered is illegal. In this way, the use of selected toxic chemicals is prevented. [27]

The policy initiatives just mentioned involve measures to avoid environmental pollution or damage to human health. They are good examples of the present view on policy making, i.e. a focus on foresight and prevention. It shows that there is a need to develop tools for ex-ante assessments. The focus of this thesis will be on ex-ante technology assessment and will focus on environmental and economic aspects in the entire life cycle of products¹. The evaluation of environmental and economic aspects throughout the life cycle of products has become standardized as ‘Life Cycle Assessment (LCA)’ and ‘Life Cycle Costing (LCC)’ respectively. The combination of these two methods is referred to as ‘life cycle engineering’² [28]. Life cycle engineering is a type of technology assessment that has evolved in the last four decades. The concept of life cycle engineering will be explained in the following paragraph.

1.3 Life cycle engineering – principles and outline

Around 1970, the first studies appeared on the environmental burden of products taking into account the entire life cycle. It was at a conference in 1991 that a decision was actually made that the name of this concept should be ‘Life Cycle Assessment (LCA)’. By 1997, the International Organisation for Standardization issued the first standard for LCA methodology (ISO 14040) [29]. By analogy with LCA, life cycle costing (LCC) is a methodology to analyze costs throughout the life cycle of a product [30]. Often these analyses are conducted in order to make a fair comparison between different alternatives by taking into account the entire life cycle³ but also to identify the processes that require special attention, because they contribute significantly to either environmental impacts or costs. The focus of life cycle engineering is to improve a product’s performance taking into account the entire life cycle.

¹ Although ex-ante assessments, the analyses in this study differ from CTA in that we do not have actors participating in the technology design and development practices.

² Recent developments involve also social assessments. However, the methodology for social assessments has not yet been fully developed let alone standardized. It is therefore not included in this thesis.

³ If a product has particularly high impacts in the production phase, but has a very high lifetime in the use phase, impacts over the entire life cycle could still be very favorable compared to a product that has lower impacts in the production phase, but also has a much lower lifetime.

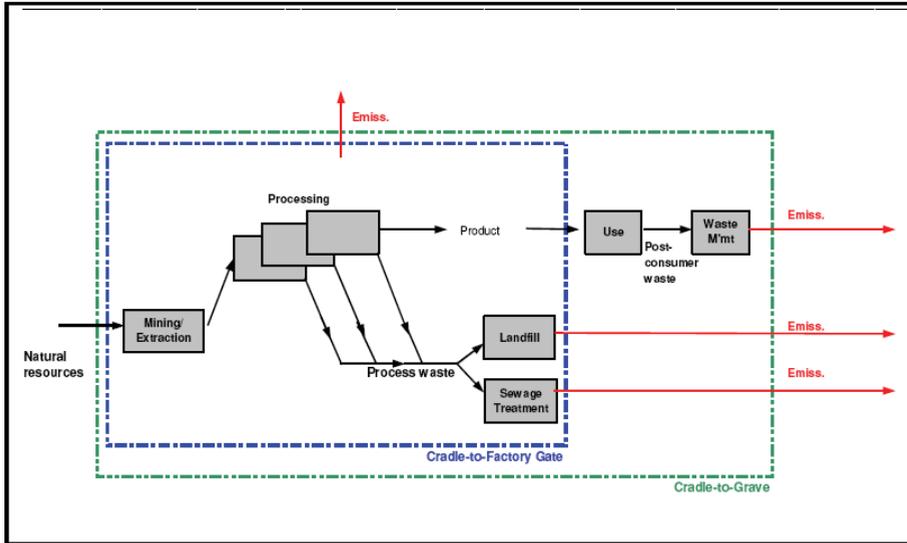


Figure 1.3: Stages and system boundaries in the life cycle of a product.

The life cycle of a product or service includes the various stages of production, use and waste management (see Fig. 1.2). The stages are:

1. Raw material extraction
2. Processing
3. Use phase
4. Waste management

A common feature of life cycle approaches for economic and environmental assessments is that they include several or all of the stages shown in Fig. 1.3. Two different systems are generally chosen to assess products, namely “*cradle-to-factory gate*” (including stages 1 and 2) and “*cradle-to-grave*” (all stages; see Fig. 1.3). Both LCA and LCC are conducted with the purpose of assessing environmental and economic impacts in *quantitative* terms. Life cycle engineering integrates LCA and LCC. The key research questions to be answered in the course of an LCE study are:

- What is the environmental and economic burden of a new product/service throughout its life cycle?
- Is the new product/service better than the traditional/existing one?
- Which steps in the process chain contribute most to environmental and economic impacts?

- Which measures can be taken to reduce the environmental impacts and the costs throughout the life cycle?

1.3.1 Life cycle assessment

The LCA methodology has been specified in a series of International Standard Organization (ISO) standards: 1) ISO 14001 [31]; 2) ISO 14040 [32] and 3) ISO 14044 [33]; Report 1 is an introduction to environmental management system, report 2 defines the principle of the method, while report 3 explains the phases of the procedure (it replaces the old ISO standards 14041, 14042 and 14043). A number of published guidelines and textbooks help the practitioner in the LCA preparation, e.g. [29, 34].

The preparation of an LCA study is divided in several phases (see Fig. 1.4):

- Goal and scope definition
- Inventory of relevant inputs and outputs of a product system
- Evaluation of potential environmental impacts associated with those inputs and outputs
- Interpretation of the inventory and assessment of the impacts in relation to the objectives of the study

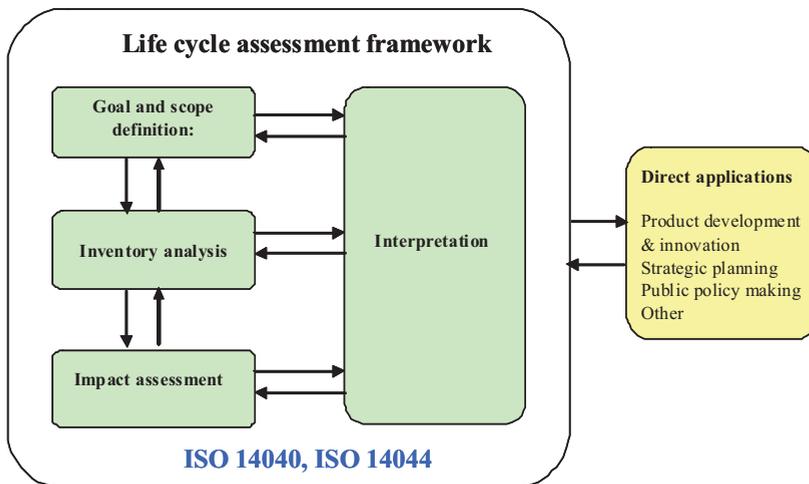


Figure 1.4: LCA framework [32,33].

Goal and scope definition

According to ISO standards, goal and scope definition can be subdivided in:

- Purpose of the analysis
- Functional unit definition
- Definition of the system
- Selection of the impacts to be evaluated

The goal and scope phase is crucial, since it clarifies which data are required for the analysis. The purposes of an LCA study are to provide i) decision support for R&D agendas in research institutes, companies and governments; ii) indications about needs and possibilities for process improvements; iii) information for marketing purposes. According to ISO standards (ISO 14044) the functional unit (FU) is the measure of the performance of the functional output of the product system and it provides a reference to which the inputs and outputs can be related. The FU can be specified in many different ways, depending on the purpose of the study. By defining the system for an LCA study it is determined which unit processes should be included in the LCA. The choice of system boundaries is determined, among other aspects, by the intended application of the study, the assumptions made and the intended audience. As a final step it is decided which impact categories (see below) are taken into account in the assessment.

Inventory analysis

The life cycle inventory analysis involves data collection and calculation procedures to quantify the total product system's inputs from and its outputs to the environment. These inputs and outputs can include resource use, atmospheric emissions, aqueous emissions, solid waste and land use.

Life cycle impact assessment

An important goal of the life cycle impact assessment is to aggregate outputs with comparable effects (e.g. all greenhouse gases or all acidifying components) by use of so-called characterisation factors. This leads to a limited number of parameters, called impact categories. These impacts can be 'mid-point'- indicators, such as non-renewable energy use, global warming, acidification or terrestrial eco-toxicity, or 'end-point' – indicators, which refer more generally to 'resource use', 'human health' or 'ecological consequences'. The mid-point indicators have then been aggregated.

The indicators can be 'weighted' in an impact assessment to give them less or more importance compared to other indicators. As an optional step, the results by impact categories can be divided by a reference value (e.g., total greenhouse gas emissions of a country) in order to better understand the relative importance of the various impacts; this step is referred to as normalisation. Weighting and normalization are related to policy preferences.

Interpretation of the results

The life cycle interpretation is the final step of the LCA where conclusions are drawn from both the life cycle inventory analysis and the life cycle impact assessment or, in the case of life cycle inventory studies, from the inventory analysis only. As an outcome of the interpretation stage, recommendations can be formulated which, for example, may be directed to producers or policy makers. Examples of such recommendations are to invest in product A instead of B, or to study energy reduction potentials in a certain production step if it has shown to be very energy intensive.

1.3.2 Life cycle costing

Life Cycle Costing (LCC) is the economic assessment of all monetary flows that are caused by a product or a service. All costs incurred along the life cycle are taken into account, from the extraction of the required resources, via the use phase to the end-of-life (waste management). We can define the following phases of the LCC, similar to those already described for LCA [30]:

- Goal and scope definition
- Cost calculations
- Interpretation of the results

Goal and scope definition

In order to quantify correctly the monetary flow, we need to define a functional unit and choose the boundaries of the system, as done in LCA. The considerations discussed in the LCA chapter are still valid; the functional unit should allow fair comparison of the various options.

Cost calculations

As in LCA, all stages in the life cycle of a product or service are also accounted for in an LCC. The cost analysis performed in each of these life cycle stages of the LCA essentially follows standard business economics.

Interpretation of the results

Life cycle costs, i.e. the sum of all the costs related to the product or service, should be minimized in order to cause lowest overall cost to the consumer. Contribution analysis helps to identify the processes that are most relevant for the overall cost. Improving the economics of these processes will reduce significantly the overall cost. For example, if LCC identifies the flame production process of nanoparticles to be the most relevant for

overall cost, the first interventions should be done on this process. Sensitivity analysis can be applied in addition to the contribution analysis in order to quantify the improvement in the economics of the product when a key parameter is changed (i.e., the efficiency of nanoparticles production in a flame process).

1.4 Focus of this thesis

At this moment, life cycle engineering is still in an early stage, since the first standards for life cycle assessment have been set only in 1997 and for life cycle costing only in 2008. In some cases the existing methods do not yet fully offer the possibility to assess technologies on all relevant aspects. Especially for ex-ante assessments, which focus on future or emerging products or technologies, there are several issues for which the LCE methodology does not provide sufficient tools for a comprehensive analysis. As we will discuss below, this concerns for example the estimation of life cycle data for the future, large scale application of technologies or products that are still in the laboratory stage. In this thesis, we will try to contribute to the following general research question:

How could the existing methodology of life cycle engineering be improved or extended to allow a more comprehensive ex-ante assessment of new technologies and what problems or uncertainties still need to be resolved?

The focus of this thesis will be on the ex-ante assessment of two novel technologies, i.e. nanotechnology and white biotechnology. These two technologies are considered as very important technologies in chemical manufacturing industry and material science with huge potentials for the future (both are sometimes referred to as technologies causing a 'revolution' in science and society). For white biotechnology, it is very important that risks to human health are identified in an early stage. At this moment, existing impact assessment methods for assessing risks to human health are insufficient. Although there are various methods that address risks/damage of emissions to human health, the risks of work-related accidents and of disasters, for example, are lacking. The development of a suitable methodology is hence required. This thesis aims at contributing to the development of such a methodology. The following subquestion is defined:

How can a generic ex-ante assessment of conventional risks be conducted for chemicals over the entire life cycle (i.e. cradle-to-factory gate plus waste stage⁴)?

This research question addresses a methodological extension of the LCA methodology with the focus on life cycle impacts. At the level of the inventory data, the LCE methodology could be improved as well: The comparison of a new product that is still in the laboratory stage with a conventional product is challenging, because life cycle data for the future, large scale application of the new product are often not available (such as for nanocomposites or polymer photovoltaics). This could be an issue in e.g. the ecodesign concept, where realistic projections need to be made for the future in order to arrive at an inventory table for future (industrial scale) product performance (such as energy and material requirements in different steps of the life cycle). An attempt is made in this thesis to contribute to this issue. The following subquestion is addressed in this thesis:

How can inventory data be estimated that represent large scale industrial practice for products or technologies that are still in the laboratory stage?

Nanotechnology offers huge perspectives for the production of new materials with enhanced properties and attributes, such as greater catalytic efficiency, increased electrical conductivity, improved hardness and strength and totally new functionalities such as self-cleaning properties. Applications are numerous (e.g. in medicine, catalysis, energy generation, ICT, aerospace, construction, refineries, consumer goods and many more). The market for products incorporating nanotechnology is estimated at \$ 1500 billion in 2010 and is expected to grow to \$ 2900 billion in 2014 [35]. Nanotechnology also has the potential to improve the environment, both through direct applications of nanomaterials to detect, prevent, and remove pollutants, as well as indirectly by using nanotechnology to design cleaner industrial processes and create environmentally responsible products [36]. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity (e.g. of free nanoobjects) and environmental impact of nanomaterials. It is therefore of great importance that the viability of this technology is assessed in an early stage, i.e. by identifying risks but also potential benefits.

White biotechnology is widely regarded as representing the next evolutionary step towards a sustainable and environmentally-friendly chemical manufacturing industry.

⁴ The inclusion of the use phase of a chemical is complicated because most chemicals can have numerous applications with different performances in the use phase. Therefore, the use phase is not taken into account.

White biotechnology can create industrial products that are more easily degradable, require less energy, create less waste during production and sometimes perform better than products created using traditional chemical processes. Although white biotechnology is not new (it has been used for the creation of, for example, food nutrients or washing powders for many years) there are several factors that have made white biotechnology more important than ever. These include recent advances in the fields of genomics, molecular genetics, metabolic engineering and catalysis combined with advances in enzyme and fermentation technology. Besides there are external factors such as soaring energy prices, renewed environmental concerns and energy security fears. [37-39]. The use of biotechnology for the production of food, however, has shown that there is large public resistance due to unknown risks associated to it. It is therefore of great importance that risks associated to white biotechnology are identified.

Given the importance of nanotechnology and white biotechnology as emerging technologies and the need for the early assessment of chances and risks of these technologies, this thesis tries to answer the following research questions:

What are the chances and risks of nanotechnology from an environmental and economic perspective, focusing on polymer nanocomposites and polymer photovoltaics?

What are the chances and risks of white biotechnology, taking into account risks to human health and focusing on the bio-based production of polytrimethylene terephthalate (PTT), polyhydroxyalkanoates (PHA) and ethanol?

In Chapter 2 an environmental and economic assessment is carried out for a polypropylene nanocomposite. This novel material is used for the production of packaging film, greenhouse film and car panels and replaces (neat) polypropylene, (neat) low-density polyethylene and glass fiber-reinforced polypropylene respectively. In Chapter 3, the environmental benefits of using nanoobjects to reinforce polymers (i.e. the production of nanocomposites) are studied by determining the ‘functionality-based non-renewable energy use’ of twenty-three different nanocomposites in relation to unreinforced polymers or conventionally reinforced polymers. Chapter 4 deals with toxicity aspects of nanoobjects and the risk that nanoobjects are released to the atmosphere after municipal solid waste incineration of nanocomposites. In Chapter 5 an environmental and economic assessment is carried out for a polymer photovoltaic (PV) system (both a system on glass and a flexible system) and compared to a multicrystalline silicon PV system (also a limited comparison to thin film systems and dye-sensitised systems is made). Chapter 6 deals with white biotechnology. In this chapter, the risks to human health are assessed for the bio-based production of polytrimethylene terephthalate

(PTT), polyhydroxyalkanoates (PHA) and ethanol and compared to the petrochemical production of these chemicals. For PHA, the bio-based production is compared to polyethylene terephthalate (PET) and polyethylene (PE). The focus is on conventional risk, i.e. risks of well established processes (risks of genetically modified organisms are excluded). Chapter 7 contains the main conclusions of this thesis.

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CHAPTER 2

Environmental and cost assessment of a polypropylene nanocomposite

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Abstract

This paper describes a study on the use of a polypropylene (PP)/layered silicate nanocomposite as packaging film, agricultural film, and automotive panels. The study's main question was 'Are the environmental impacts and costs throughout the life cycle of nanocomposite products lower than those of products manufactured from conventional materials?' The conventional (benchmark) materials studied were pure polypropylene as packaging film, pure polyethylene as agricultural film, and glass fiber-reinforced polypropylene as automotive panels. In all three cases, the use of the PP nanocomposite resulted in a reduction of the amount of material used, while ensuring the same functionality. Material reduction was estimated using Ashby's material indices and amounted to 9% for packaging film, 36.5% for agricultural film, and 1.25% for automotive panels.

It goes without saying that a product's impact on the environment will decrease when less material is used. The production and incorporation of nanoparticles, however, may have additional impacts. We found clear environmental benefits throughout the entire life cycle when the PP nanocomposite is used in the manufacture of agricultural film. We noted some cost benefits when the nanocomposite is used in the production of agricultural film and automotive panels. If the price of nanoclay is at most €5000/tonne, then the cost of nanocomposite packaging film is also lower than that of the conventionally produced product.

2.1 Introduction

Nanotechnology is a very promising field for industrial applications. In fact, several products are already on the market for certain niche sectors with high added value, e.g., biomedical materials and analytic devices. The real revolution in nanomaterial applications, however, is expected to involve widely used bulk products. Polymers like polyolefins and polyvinylchloride (PVC), for example, are good candidates in this respect because of their large-scale use and versatility. Indeed, one of the first applications of nanotechnology was the production of nanofillers for the improvement of the mechanical properties of polymers [1-3]. Polypropylene (PP) is particularly interesting because of its low cost and good mechanical properties. This polymer has been used in conventional composites for a long time and, in combination with nanofillers, shows better mechanical properties with even low amounts of filler. The main nanofillers used today are nanoclay (natural product) and carbon nanotubes (synthetic). Synthetic carbon nanotubes are very expensive. Nanoclays (layered silicates), in contrast, are especially interesting for bulk applications because they are relatively inexpensive and they cause an improvement in the mechanical properties of polymers. Commonly used nanoclays include montmorillonite, hectorite, and saponite, all of which belong to the same general family of 2:1 layered or phyllosilicates [4].

The addition of nanoclay increases not only the elasticity and strength of PP, but also its barrier and fire-retardant properties. In applications such as structural elements and films, these improved mechanical properties allow a reduction of the quantity of material in a specific product. As a result of the material reduction, the environmental impact of PP nanocomposite products can be expected to be lower than that of products made out of conventional material unless the production of the nanoparticles is accompanied by particularly high environmental impacts. The overall effect of nanocomposite products needs to be evaluated by means of a methodology that includes all of the steps of the life cycle: life cycle assessment (LCA).

Analogous to the environmental effects, a reduction in mass is also likely to affect the overall cost of nanocomposite products. Life cycle costing (LCC) is a methodology similar to LCA that allows the assessment of product costs throughout the life cycle.

Since this study deals with products that are still in the research or early production stage, a comprehensive evaluation of all environmental impacts and costs was not possible. Prospective forms of LCA and LCC can, however, be used to arrive at indicative results. These outcomes can then be used to make any necessary alterations in the production phase and to improve the efficiency of the processes.

The goal of the present study was to conduct prospective LCA and LCC of PP/layered silicate nanocomposite products. Three representative products were investigated: thin

film for packaging, thick film for agricultural use, and injection-molded panels used in cars. Data from both the literature and industry were used to estimate the reduction in mass of the nanocomposite products, compare it to that of conventional products, and evaluate the environmental and cost (dis-)advantages. In 2003, Lloyd and Lave [5] studied nanocomposite automotive panels. We believed that we could significantly enhance their work using a different approach. Lloyd and Lave used steel and aluminum car panels as a reference, while we focused on PP panels. Both studies used Ashby material indices [6] to estimate mass reduction. However, our estimates for the Young modulus that are used in Ashby's material indices, were derived from experimental data, while Lloyd and Lave used an idealized model from Brune and Bicerano [7] that is subject to substantial uncertainty by assuming perfect adhesion between the clay platelets and the matrix. In the LCA part of the study, we used LCA databases (e.g., Ecoinvent) that are based on measured inputs and emissions of discrete industrial processes (e.g., per kg or MJ of product). Lloyd and Lave, in contrast, applied a hybrid method which derives environmental impacts from the economic output of the respective sector or subsector and is hence less accurate.

2.2 Environmental assessment: Life cycle assessment

2.2.1 LCA fundamentals

Life cycle assessment (LCA) is a standardized method for the compilation and evaluation of the inputs, outputs, and potential environmental impacts of a product system throughout its life cycle. LCA methodology was standardized in 1997 by the International Standardization Organization (ISO) in their ISO-14040 series [8]. This standard distinguishes the following steps:

1. *Goal definition and scoping.* This step defines the purpose and the methodology of the LCA. Frequently, this is a comparison between two or more product alternatives. The product systems to be evaluated are defined together with the geographical and the temporal scopes. This phase also includes the definition of the functional unit, which then acts as a reference for the following steps. Finally, it determines which environmental impacts must be taken into account (the choice should be as comprehensive as possible).
2. *Inventory analysis.* In this phase, a flow diagram is developed and all energy and material requirements, emissions to air, water, and soil, and other environmental releases are quantified.
3. *Impact assessment.* This assessment determines the (potential) environmental impacts caused by the environmental releases analyzed in the inventory analysis.

4. *Interpretation*. In this final step, the results of the inventory analysis and the impact assessment are discussed, conclusions are drawn, and recommendations are made.

2.2.2 Goal definition and scoping

The purpose of the LCA in the present study was to investigate whether the use of a polypropylene nanocomposite has environmental advantages over the use of conventional polyolefins. To this end, we studied three product systems, namely packaging film, agricultural film, and automotive panels. The three conventionally produced products are all made of different materials: the packaging film is made out of neat PP, the agricultural film out of neat polyethylene (PE), and the automotive panels out of glass fiber-reinforced PP. A prospective LCA was performed (cradle-to-grave) that covers a wide range of environmental impacts. Using the LCA databases from SimaPro [9], we conducted an impact assessment on non-renewable energy use (NREU), climate change (Global Warming Potential, GWP_{100}), abiotic depletion, ozone layer depletion, photochemical oxidant formation, acidification, and eutrophication. We did not take into account *human toxicity*, *terrestrial ecotoxicity*, *marine aquatic ecotoxicity*, or *fresh water aquatic ecotoxicity*, because the existing methods do not yield comparable results and because they are incomplete with regard to the emissions studied [10].

2.2.2.1 Characteristics of the functional units

A functional unit was defined for each of the products studied. They are listed below together with the weights of the conventional products. The weights of the nanocomposite products are discussed in Section 2.2.2.2.

Packaging film: As the functional unit, we chose the amount of packaging film needed for 1000 bags of 200 g “Fruitfante” candies produced by Schuttelaar B.V. (Waddinxveen, The Netherlands). The function of these bags is to provide sufficient physical protection and to act as a barrier in order to preserve the candies. Pure PP is the conventional material used to produce such a bag. We compared it with film produced from a PP nanocomposite.

Product characteristics of *conventional* packaging film:

- Weight of one bag⁵: 3.66E-03 kg
- **Film requirement for functional unit: 3.66 kg**

⁵ Weight of a packaging bag was based on: thickness of film = 6.00E-05 m; length of bag = 0.214 m; width of bag = 0.157 m; density of PP = 0.91 t/m³; 2 sheets per bag.

Agricultural film: The functional unit is the amount of plastic film needed to cover a standard tomato greenhouse with a volume of approximately 650 m³. The purpose of this film is to provide thermal insulation and UV stability, combined with the necessary mechanical strength. We considered polyethylene (PE) to be the conventional material. It is compared with an agricultural film made out of a PP nanocomposite.

Product characteristics of *conventional* agricultural film:

- **Film requirement for functional unit⁶: 2.38 t**

Automotive panel: Body panels of a low-weight family car that runs 150,000 km during its entire lifetime were chosen as the functional unit. A PP-glass fiber composite was assumed to be the conventional material and is compared with panels produced from a PP nanocomposite.

Product characteristics of *conventional* body panels:

- **Panel requirement for functional unit: 20 kg [13]**

2.2.2.2 Weight saving using nanocomposites

When a polymer (PP, PE) is blended with a nanoclay, the nanoclay silicate platelets exfoliate and bind with the polymer strands to form a nanoclay-polymer composite. This new nanocomposite structure exhibits improved material properties. The silicate layers have a labyrinthine effect on the diffusing gas and/or liquids, which leads to improved barrier properties. This makes nanocomposites an interesting class of materials for the packaging industry and for all applications in which low permeability is required. Moreover, the labyrinthine effect is supposedly involved in the improvement of fire-retardant properties [14]. Several studies have shown that mixing a polymer with nanoclay also improves its elasticity (Young modulus-E) and strength (tensile strength- σ_t) [3, 15-21]. When material properties like barrier properties, strength, and elasticity improve, less material is needed to fulfill the same function. This means that the weight of the nanocomposite product will be lower than that of the conventional material.

In order to estimate the amount of nanocomposite material required for a given function, its properties must be compared with those of conventional materials. To do this, Ashby [6] defined material indices for different product functions (e.g., beam or panel) which have to comply with certain requirements, e.g. stiffness, strength, and tolerance to

⁶ Weight of agricultural film was based on: thickness of film = 0.006 m; length of greenhouse = 29.26 m; width of greenhouse: 7.00 m; width of greenhouse roof film = 8.00 m; height of greenhouse = 2.44 m; density of film = 0.92 t/m³ [11,12].

vibration. He based these material indices on material properties like the Young modulus (E), tensile strength (σ_f), and density (ρ). Using these indices, a nanocomposite material can be compared with conventional material with regard to mechanical properties. This allows estimation of material (weight) reduction. We chose the following equations from the various material indices distinguished by Ashby:

Packaging film and agricultural film:
$$MI = \sigma_f / \rho \quad (1)$$

We assumed:

- Strength-limited (the material should not tear)
- Tie (tearing is caused by a force parallel to surface of the film)

Automotive panels:
$$MI = E^{1/3} / \rho \quad (2)$$

We assumed:

- Stiffness-limited (the material should not bend, it should be stiff)
- Panel

Ashby's material indices are inversely proportional to the amount of material needed for a given function: i.e., the higher the index, the less material is needed for the same function. Weight saving as a result of nanocomposite use can now be estimated.

For *packaging film* and *agricultural film*, weight saving was calculated using:

$$\text{Change of weight (\%)} = \left(\frac{\sigma_f / \rho [\text{conv}]}{\sigma_f / \rho [\text{nano}]} - 1 \right) \bullet 100 \quad (3)$$

For *automotive panels*, weight saving was calculated using:

$$\text{Change of weight (\%)} = \left(\frac{E^{1/3} / \rho [\text{conv}]}{E^{1/3} / \rho [\text{nano}]} - 1 \right) \bullet 100 \quad (4)$$

Ashby's method allows one to compare materials for a given purpose on the basis of their mechanical properties. When studying packaging film, this is not, however, the only aspect that must be taken into account. The barrier properties of this material are of major importance because the food that it envelops must be preserved. An additional index,

therefore, is necessary: the oxygen transmission rate (OTR). This index reflects oxygen permeability. In order to have optimal properties, the OTR must be minimized. We estimated the material reduction due to the use of nanocomposite film by assuming that the thickness of the film is proportional to the OTR (the higher the OTR, the thicker the film must be). That is, we calculated the weight saving using:

$$\text{Change of film thickness (t, \%)} = \left(\frac{OTR [nano]}{OTR [conv]} - 1 \right) \bullet 100 \quad (5)$$

$$\text{Change of weight (\%)} = \left(\frac{\left(\frac{t}{100} + 1 \right) \bullet \rho[nano]}{\rho[conv]} - 1 \right) \bullet 100 \quad (6)$$

The values for tensile strength (σ_f), Young modulus (E), oxygen transmission rate (OTR), and specific weight (ρ) used in this study are listed in Table 2.1.

Parameter	Value	Unit	Reference
σ_r - PP	33.5	MPa	[22]
σ_r - LDPE	24	MPa	[12]
σ_r - nanocomp 3% clay (for packaging film and agricultural film)	37.4	MPa	[22]
E - PP/GF comp (30% GF)	5.76	GPa	[23]
E - nanocomp 5% clay (for automotive panels)	1.8	GPa	[22, 23]
OTR - PP	95	(cc.mm) / (m ² .24h.1 Atm)	[23]
OTR - nanocomp 3% clay	76.9	(cc.mm) / (m ² .24h.1 Atm)	Expert estimation and [23]
ρ - PP	0.91	t/m ³	
ρ - LDPE	0.923	t/m ³	
ρ - nanocomp 3% clay	0.928	t/m ³	
ρ - nanocomp 5% clay	0.94	t/m ³	
ρ - PP/GF comp	1.402	t/m ³	

Table 2.1: Parameter values (LDPE: Low-density polyethylene, Nanocomp: Nanocomposite, PP/GF comp: Polypropylene/glass fiber composite).

Inserting these values in Equations (3)-(6) resulted in the estimates for weight saving listed in Table 2.2. Applying this weight reduction to the functional units based on conventional material yielded the weight of the products made with the polypropylene nanocomposite.

	Weight of functional unit with conventional material	Weight saving	Formula used	Weight of functional unit with nanocomposite
Packaging film, based on OTR	3.66 kg	-17.5%	Eq. (6)	3.02 kg
Packaging film, based on mechan. properties	3.66 kg	-9%	Eq. (3)	3.33 kg
Agricultural film	2.38 t	-36.5%	Eq. (3)	1.51 t
Automotive panels	20.00 kg	-1.25%	Eq. (4)	19.75 kg

Table 2.2: Estimated weight saving when polymer nanocomposites are used.

Table 2.2 shows that the weight-saving estimation for packaging film is -17.5% based on OTR. However, because its mechanical properties (σ_t) do not allow a weight saving of this magnitude, the maximum weight saving for packaging film is -9%. This value was used in further calculations of packaging film. The weight saving for agricultural film is four times higher than for packaging film. This is caused by the large difference in tensile strength between the nanocomposite and low-density polyethylene (LDPE, conventional material used). The weight reduction for automotive panels is more or less negligible (-1.25%). Although there is no improvement in the Young modulus when nanocomposites are used, there is a large improvement in density. The lower density is also the reason for the weight reduction. Calculating weight savings by hand using the values in Table 2.1 gave slightly different values than reported in Table 2.2. This was due to rounding-off errors.

2.2.3 Inventory analysis

2.2.3.1 The life cycle

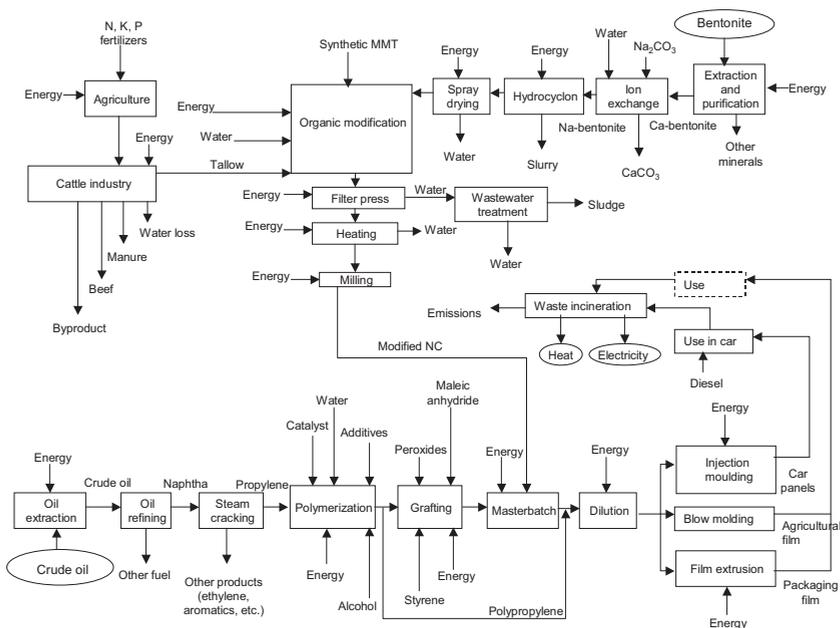


Figure 2.1: Process chain for the production and use of polypropylene nanocomposite products.

Figure 2.1 shows the process chain for the production of polypropylene nanocomposite products, i.e. packaging film, agricultural film, and automotive panels. To the authors' knowledge, the production process shown in the figure has not yet been operated on a commercial scale. Since we studied the process in an early stage, there is room for optimization. In fact, our assumptions may be too conservative, i.e. more substantial progress than assumed might be possible with regard to material properties (see below). Moreover, other process configurations, possibly involving other types of nanoparticles, may turn out to be more attractive.

The life cycle process of a nanocomposite comprises five major steps: the preparation of the nanoclay, the preparation of polypropylene, the mix/dilution step, the use phase, and the waste treatment phase. In the nanoclay part of the process, raw clay (Ca-bentonite) is extracted and subjected to an ion exchange to replace divalent calcium ions with

monovalent sodium ions. This results in an increase in the interlayer distance between the clay platelets. After separation (“hydrocyclone”) and a drying step (“spray drying”), another ion exchange is performed (“organic modification”) in which sodium ions are replaced by alkyl quaternary ammonium salts (delivered by tallow), which increases the interlayer distance even more. The distance between the platelets is a crucial factor during composite preparation since it helps achieve a sufficient degree of dispersion of the nanoclay in the PP matrix. This dispersion is accomplished during the preparation of the so-called masterbatch in an extruder (the shearing force applied leads to dispersion) after the clay particles have been filtered (“filter press”), dried (“heating”), and ground to reduce particle size to about 30 μm (“milling”).

The preparation of polypropylene starts with crude oil. Crude oil is refined after its extraction and one of the products is naphtha, which is steam-cracked. One of the main outputs of this steam-cracking process is propylene, which is then polymerized to polypropylene.

In the mix/dilution step the polypropylene is first grafted with maleic anhydride. This compound acts as a compatibilizer that helps blend the polypropylene and the clay, and lead to better mechanical properties [15,18]. Then, in the masterbatch, the grafted polypropylene is mixed with the modified nanoclay to obtain the nanocomposite. To acquire the desirable nanoclay concentration, extra polypropylene is added in the dilution step. The final product is achieved by either film extrusion (packaging film), blow molding (agricultural film), or injection molding (automotive panel).

The next step of the life cycle is the use phase. In the case of automotive panels, for example, the use phase allows for the amount of fuel that is needed in a car based on the weight of the panels. The nanocomposite automotive panel is lighter in weight than the conventional panel and therefore results in lower petrol consumption in the use phase. There are no analogous considerations for packaging films and agricultural films. Because the conditions in the use phase for both the nanocomposite and the conventional products are identical, the use phase was not considered in the LCA. The final step of the life cycle is waste treatment. We assumed that, after disposal, the products are burned in a waste incinerator in which part of the released energy (the reaction is exothermic) is recovered for the generation of heat and power.

2.2.3.2 Life cycle inventory data

Table 2.3 presents an overview of the material and energy inputs needed for nanocomposite production and the use phase. Data for product forming are given separately in Table 2.7. Tables 2.4-2.6 show the energy and material requirements of the products in more detail (per tonne product). The values for film represent the input data for both packaging and agricultural film (identical assumptions). Data for PP came from

APME⁷ Ecoprofiles [24], while data on the production of nanoclay (Table 2.4) and nanocomposite (Table 2.5) were provided by the Institute for Polymer Research (IPF, Dresden, Germany). The latter energy and material data came from a pilot plant that produces polypropylene/nanoclay-composite film. The amount of electricity needed for extrusion (used for grafting, masterbatch, dilution, and glass fiber/polypropylene composite production) was estimated from data from the Energy Efficiency Office [25]. The energy and material inputs for the production of polypropylene-glass fiber composite are listed in Table 2.6. The material requirements were taken from Qiu et al. [26]. Silane-grafted polypropylene (PP-g-Si) was replaced by maleic anhydride-grafted polypropylene (PP-g-Ma, as for nanocomposite) because better life cycle inventory data were available for the latter compound. Table 2.7 lists the inputs for the production of the final products.

Input	Unit	Packaging film		Agricultural film		Automotive panel	
		Nanocomp. f.u.: 3.33 kg	Conv. f.u.: 3.66 kg	Nanocomp. f.u.: 1510 kg	Conv. f.u.: 2380 kg	Nanocomp. f.u.: 19.75 kg	Conv. f.u.: 20.0 kg
Polypropylene	kg	3.21	3.66	1457	-	18.6	-
Polyethylene	kg	-	-	-	2380	-	-
PP/GF composite	kg	-	-	-	-	-	20.0
Nanoclay	kg	0.1	-	45.3	-	0.99	-
Styrene	kg	0.01	-	4.53	-	0.099	-
Maleic anhydride	kg	0.005	-	2.27	-	0.049	-
Electricity for nanoclay production	MJ	2.12	-	963.5	-	21.01	-
Fuel oil for nanoclay	kg	0.010	-	4.68	-	0.10	-
Electricity for nanocomposite production	MJ	9.1	-	4146	-	57.2	-
Diesel	l	-	-	-	-	161.4	163.4

Table 2.3: Energy and material inputs for production and use of products (f.u.: functional unit, nanocomp.: nanocomposite, conv.: conventional material).

⁷ Currently known as 'PlasticsEurope'.

Inputs for production of nanoclay	Unit	Amount for 1 tonne of film	Amount for 1 tonne of panel
Bentonite ^a	tonne	0.0195	0.0325
Soda	tonne	0.002	0.0032
Tallow	tonne	0.0105	0.0175
Fuel oil			
- for spray drying	kg	3.1	5.17
Electricity			
- for ion exchange	MJ _e	0	0
- for hydrocyclone	MJ _e	18.7	31.2
- for spray drying	MJ _e	7.66	12.7
- for organic modification	MJ _e	442	737
- for filter press	MJ _e	2.2	3.67
- for heating	MJ _e	152.1	253.6
- for milling	MJ _e	15.42	25.7

Table 2.4: Energy and material inputs for the production of nanoclay for 1 tonne of film and 1 tonne of panels

a) Data for the extraction and purification of bentonite were not found. Therefore, data for kaolin were used instead [27].

Inputs for production of nanocomposite	Unit	Amount for 1 tonne of film	Amount for 1 tonne of panel
Polypropylene resin			
- for grafting	tonne	0.025	0.042
- for dilution	tonne	0.94	0.90
Maleic anhydride	tonne	0.0015	0.0025
Styrene	tonne	0.003	0.005
Peroxides	tonne	0.0006	0.001
Electricity			
- for grafting	MJ _e	75.6	126
- for masterbatch	MJ _e	151.2	252
- for dilution	MJ _e	2520	2520

Table 2.5: Energy and material inputs for the production of 1 tonne of nanocomposite for film and 1 tonne of nanocomposite for panel (without production of nanoclay - see Table 2.4).

Inputs for production of polypropylene- glass fiber composite	Unit	Amount for 1 tonne of panel
Polypropylene resin	t	0.688
Maleic anhydride	t	0.0035
Styrene	t	0.007
Peroxides	t	0.0014
Glass fiber	t	0.3
Electricity	MJ _e	2696.4

Table 2.6: Energy and material inputs for the production of 1 tonne polypropylene-glass fiber composite (the electricity requirements cover the grafting of PP and the extrusion needed to produce the composite).

Product	Inputs for the production of the products	Unit	Amount for 1 tonne of product	Reference
Packaging film - conventional	Polypropylene-oriented film	tonne	1.0	[24]
Agricultural film - conventional	Low-density polyethylene film	tonne	1.0	[24]
Automotive panel - conventional	- Polypropylene-glass fiber composite - Injection molding - Electricity	tonne GJ _e	1.0 9.11	- [26] - (According to [28], but excluding space heating)

Table 2.7: Inputs for the production of the products.

All of the nanocomposite products are produced from polypropylene nanocomposites and processed the same way as the conventional products.

When an automotive panel is used in a car, part of the car fuel use can be assigned to the panel. We used the following data:

- Weight of the car without panels: 1110 kg
- Weight of polypropylene-glass fiber panels: 20 kg
- Weight of nanocomposite panels: 19.75 kg (1.25% weight reduction)
- Fuel use during the life of the car (150,000 km) with PP/GF panels: 9804 l [29]

- Fuel use during the life of the car (150,000 km) with nanocomposite panels⁸: 9802 l
- Fuel use assigned to PP/GF panels: (20/1130)*9804 l = 173.5 l
- Using $\rho_{\text{diesel}} = 0.84 \text{ kg/l}$ gives 7.2879 t diesel/ t panel
- Fuel use assigned to nanocomposite panels (analogous to PP/GF panels): 7.2883 t diesel/t panel

After use, the products are disposed of in a waste incinerator. Energy is released during waste incineration. It is assumed that for every joule of waste (calorific value), 0.12 joules of electricity and 0.12 joules of heat are regained⁹ [30]. The calorific values of the products (the waste fractions) are listed in Table 2.8.

Material	Calorific value (higher heating value, GJ/tonne)
PP	48.9
PE	50.3
Tallow	41.88

Table 2.8: Calorific values (higher heating values) of the waste fractions.

Using the material inputs from Tables 2.4-2.6 yields the energy credits listed in Table 2.9. Note that they are valued negatively because electricity and heat are produced and the impacts of conventionally generated electricity and heat are avoided. (A representative mix of European electricity was obtained using the weighed average of UCTE, NORDEL, CENTREL, UK and IE electricity. See Table 2.10)

⁸ According to Sedan equation: $f_2 = f_1 \cdot \left(\frac{W_1}{W_2}\right)^{0.72}$, where f = car efficiency (km/kg fuel) and W = weight of the car.

⁹ These values have been updated in later studies (e.g. see Chapter 3)

Product	Electricity (GJ/tonne)	Heat (GJ/tonne)
Nanocomposite packaging film	-5.71	-5.71
Conventional packaging film	-5.87	-5.87
Nanocomposite agricultural film	-5.71	-5.71
Conventional agricultural film	-6.04	-6.04
Nanocomposite automotive panel	-5.61	-5.61
Conventional automotive panel	-4.04	-4.04

Table 2.9: Energy credits from product incineration.

The incineration process produces not only energy credits, but also emissions. These were taken into account using data from Doka [31] (see Table 2.10).

The impact assessment of all the material and energy inputs and outputs listed above was calculated using SimaPro 7 software and the following data sources (Table 2.10):

Input	Data source
Kaolin	[27]
Soda	[32]
Tallow	[33]
PP resin	[24]
Glass fiber	[34]
Maleic anhydride	[32]
Styrene	[27]
Natural gas	[35]
Electricity: weighed average of 65 % UCTE Electricity, 13% NORDEL Electricity and 9 % CENTREL Electricity, 12% UK Electricity and 1% IE Electricity (All medium voltage)	[36]
Fuel oil	[37]
Diesel, low sulfur	[37]
Polypropylene incineration	[31]
Polyethylene incineration	[31]
Output	Data source
Heat (natural gas)	[35]
Electricity (as above)	[36]

Table 2.10: Input and output references.

2.2.4 Results: Life cycle impact assessment

The life cycle impact assessment was carried out using the impact categories defined by Guinée et al. [38] and the non-renewable energy use (NREU; this is total fossil and nuclear energy). The results are presented in Table 2.11 and Figures 2.2-2.4. Note that *relative* results have been included in the figures and that they represent the difference between the conventional product and the nanocomposite product. This form of presentation was chosen, because the different units of the impact categories make it impossible to show absolute results in one graph.

Impact category	Unit	Packaging film		Agricultural film		Automotive panel	
		Nanocomp	Conventional	Nanocomp	Conventional	Nanocomp	Conventional
NREU	GJ	0.284	0.283	107.1	155.9	9.56	9.60
Climate change	kg CO ₂ -eq	15.7	15.9	5642	9242	169.1	165.7
Abiotic depletion	kg Sb-eq	0.135	0.139	52.8	79.4	4.22	4.21
Ozone layer depletion	kg CFC-11-eq	-1.83E-7	-2.81E-7	-8.32E-5	-1.88E-4	6.64E-5	6.86E-5
Photochem oxidant form	kg ethylene	3.83E-3	3.88E-3	1.21	1.16	0.067	0.068
Acidification	kg SO ₂ -eq	0.116	0.12	36.5	38.7	1.381	1.395
Eutrophication	kg PO ₄ ³⁻ -eq	8.62E-3	9.19E-3	2.78	4.37	0.123	0.124

Table 2.11: Impact results for nanocomposite and conventional packaging film, agricultural film, and automotive panels.

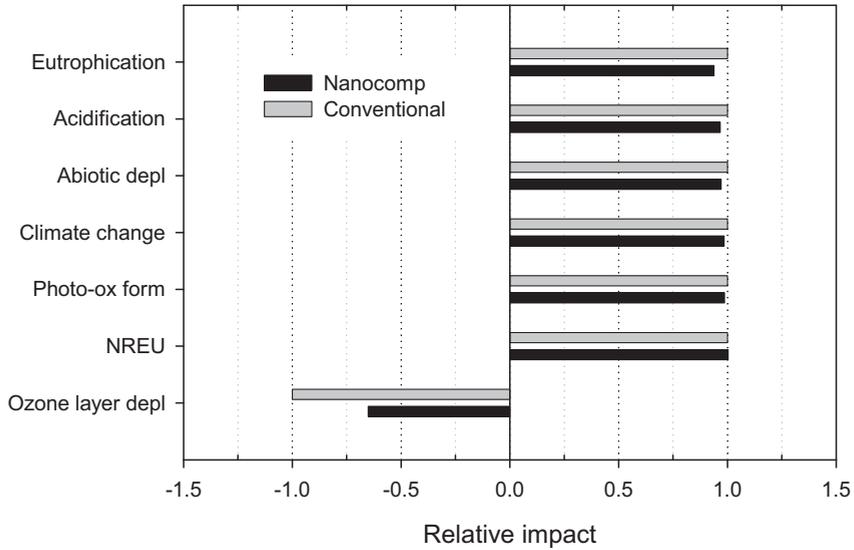


Figure 2.2: Relative results of the impact assessment of packaging film.

Figure 2.2 shows that both product alternatives are more or less equal for all but the ozone layer-depletion impact (the differences are less than 6%). The impact of the ozone layer depletion differs from those of the other impacts in that it is negative. The reason for this is that the credits from waste incineration outbalance the impacts of the other life cycle stages. Due to its lower PP content, the nanocomposite packaging film has fewer credits than the conventional product. One can conclude, therefore, that the conventional product is somewhat better for the environment with regard to the ozone layer depletion impact.

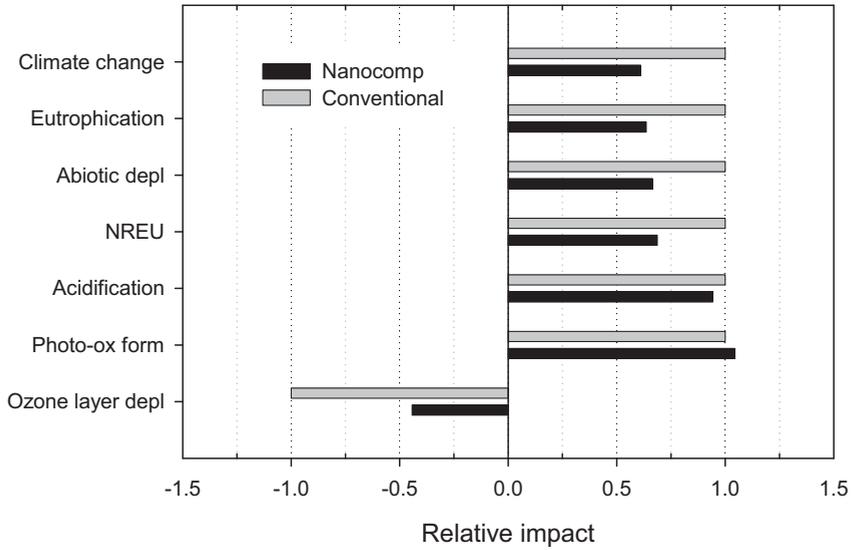


Figure 2.3: Relative results of the impact assessment of agricultural film.

Figure 2.3 shows that nanocomposite agricultural film has a lower impact for most of the categories. With regard to photochemical oxidant formation, however, the impact of the nanocomposite is somewhat higher. Credits with regard to waste incineration are higher for the conventional product than for the nanocomposite (due to the higher weight of the conventional product). Nonetheless, the overall conclusion is that the nanocomposite performs better in environmental terms than the conventional product.

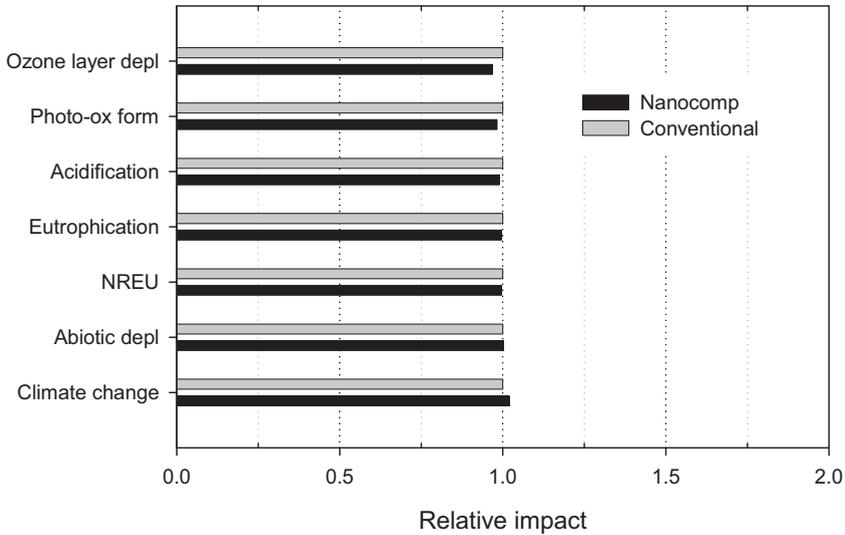


Figure 2.4: Relative results of the impact assessment of automotive panels.

It can be concluded from Figure 2.4 that both product alternatives of automotive panels perform more or less equally for all impacts (between -3% and +2% difference).

2.2.5 Discussion and conclusions: Life cycle interpretation

The main differences in life cycle impact between conventionally produced products and products made from a polypropylene nanocomposite could be the result of 1) the production of nanoclay in the nanocomposite products and 2) the reduced weight of the nanocomposite products.

Although the use of nanoclay in nanocomposite products might be expected to cause a major difference, it is generally of minor importance due to the very low clay load of the composites. The fact that uncertainties in life cycle inventory (LCI) data of nanoclay production are high (they are based on estimates and pilot plant laboratory data) does not, therefore, impair the robustness of the results. The real impacts of nanoclay production are probably even lower than estimated in this study, because the energy use in the pilot plant considered here is probably higher than the energy use in commercial-scale industrial plants.

Besides the nanoclay production, further impacts are related to composite preparation, polymer production, product forming, waste incineration, and, in the case of automotive panels, diesel consumption in the use phase. Overall, diesel consumption in the use phase is an important contributor to the life cycle impacts of the automotive panel. Figure 2.5 shows that, with respect to non-renewable energy use, diesel consumption is the main contributor.

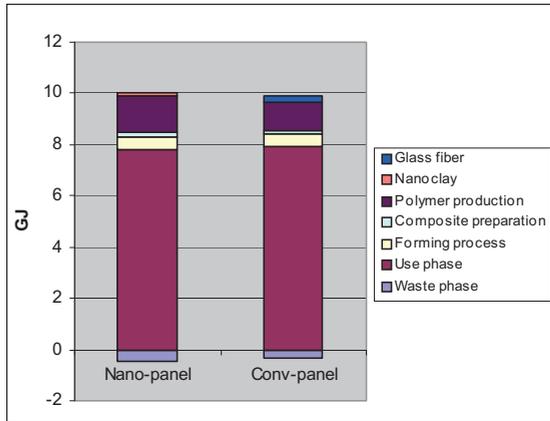


Figure 2.5: NREU of 1 functional unit of automotive panels (cradle-to-grave).

The estimated weight reduction was highest for agricultural film, namely -36.5%. Figure 2.6 shows that this results in a clearly lower environmental impact of the nanocomposite.

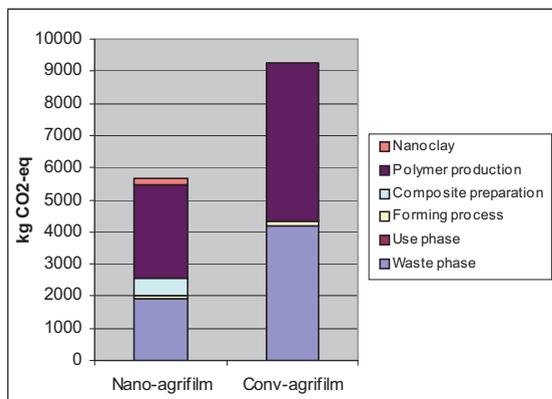


Figure 2.6: Climate change of 1 functional unit of agricultural film (cradle-to-grave).

Data on polypropylene and polyethylene production, oriented film production, and film extrusion were taken from APME Ecoprofiles [24]. These data, from industrial plants, were gathered in the early 1990s and are, therefore, somewhat dated. Although more recent (2005) data have been made available by this research group [28], the 2000 data [24] have a much higher level of detail, especially for lower material inputs and emissions. Because this enables a more precise impact assessment, data from the 2000 publication [24] were used in the present study. A general comparison between the processes described in the two APME Ecoprofiles studies [24, 28] showed that the contribution to non-renewable energy use decreased by around 3% and that the contribution to climate change has not changed in the last years. It is plausible, therefore, that the old data still give a good estimate of the present environmental impacts of polymer production and product forming and that there have only been marginal improvements in the last years.

With respect to the CML 2 baseline 2000 method [38], it should be emphasized that not all inventory data were converted to impact. This is due to incomplete coverage of the method as a result of knowledge gaps. In fact, there are important information gaps, especially with regard to toxicity (eco- and human), and the outcome depends strongly on the method used. These toxicity impacts, therefore, were excluded from the present study (they are not incorporated in Figures 2.2-2.4). Methods for determining the (eco)toxicological impacts of products are, however, improving; for example, progress was reported in the LCA project OMNIITOX [39, 40].

Impacts are considered to be more precise for NREU and climate change, because the entry commodities from which they are calculated are considerably less than for toxicity

and because they can easily be derived from measured data (e.g., from metered power use). The main reason nanocomposite product alternatives are expected to have lower environmental impacts is because less material is needed for the same function. The method we used to estimate weight reduction, however, is subject to uncertainty. Important questions to be raised are: 1) Does the application of Ashby's method lead to sufficiently accurate results for the products under consideration? 2) If so, what are the best estimates for the material properties E and σ ? These questions will be dealt with in the following paragraphs.

The use of Ashby's material indices for the environmental assessment of nanocomposites was first applied by Lloyd and Lave [5], who used them to estimate the weight reduction of nanocomposite automotive panels. We used the same formula in the present study: $M = E^{1/3}/\rho$. This formula was derived from the assumption that panels are stiffness-limited. However, also with respect to packaging and agricultural films, which are assumed to be strength-limited, the Ashby indices provide just a preliminary analysis. A thorough study is required for a more accurate estimate.

Many investigations have reported different values for E and σ . Our estimations of the two properties are uncertain as well. We used data from Svoboda et al. [22], who reported a smaller increment in E and σ when using nanocomposites than did, for example, Kretzschmar et al. [17] and Oya et al. [19]. Kretzschmar's group [17] used neat PP with a very low value for E and σ . The beneficial effect of adding nanoparticles is known to be more pronounced for this type of material, i.e., the increase in E and σ is higher. Based on personal communication from experts in the field, however, we believe that a small increase in E and σ is more realistic. Whatever the case, our approach leaves room for the possibility that our weight-reduction estimate is too pessimistic and that the advantages of using nanocomposites are better than what we report here.

We assumed the uncertainty to be smaller for agricultural film because the σ value of polyethylene came from a greenhouse film supplier [12] and the value of the nanocomposite was in line with other sources.

There was a large variation among the data sources with respect to the oxygen transmission rate (OTR). We used field data in combination with data from MatWeb [23] to study this factor. According to our calculations, the limiting factor for weight reduction comprises mechanical not barrier properties. The uncertainties with regard to the oxygen transmission rate, therefore, are less relevant as long as the mechanical properties are the limiting factor.

Using the assumptions we made in this study, we were able to conclude that the use of a polypropylene nanocomposite *can* have clear environmental advantages over conventional material in certain cases.

- Our results were best for agricultural film since the use of a nanocomposite showed a lower impact for five out of seven environmental categories. This was the result of the high weight saving.
- The impact of the nanocomposite on packaging film was similar to that of neat polypropylene. The nanocomposite did, however, have a higher impact on ozone-layer depletion.
- The nanocomposite automotive panel and conventional automotive panel performed equally well.

2.3 Economic assessment: Life cycle costing

2.3.1 Methodology

In contrast to LCA methodology, life cycle costing (LCC) has not yet been standardized. The Society for Environmental Toxicity and Chemistry (SETAC) is, however, currently working on the matter [41]. Like those described above for LCA, the following phases can be defined for LCC:

- Goal and scope definition
- Cost calculations
- Interpretation of the results

2.3.2 Goal and scope definition

Although the focus is on economic aspects, the goal and scope of the LCC in this study are similar to those of the environmental assessment reported in the first part of the article. The coverage is also cradle-to-grave.

2.3.3 Cost calculations

The costs of manufacturing the products under consideration were estimated using the market prices of all material and energy inputs. The relevant inputs are listed in Table 2.3. Peroxides were not taken into account due to a lack of price data. Moreover, the amount of peroxides in the final product is negligible (no more than 0.1%).

Life cycle costs were calculated from the material and energy inputs and their costs. Note that the prices vary over the years and differ per source. The price of polypropylene, for example, is closely correlated to that of crude oil due to the use of oil-based feedstocks, the process energy necessary for the production, and the limited number of process steps. As a consequence, the polypropylene price was higher in 2005 than in 2000. We assumed

the same relationship for the prices of the other petrochemical inputs (LDPE, styrene, and maleic anhydride). As a result, we defined the price ranges shown in Table 2.12.

The price range for nanoclay was based on estimates from various sources, while the price range for the PP-glass fiber composite was an estimate from Wageningen University and Research Centre [42].

	Low price	High price	Unit	Source
Nanoclay	4400	10000	€/tonne	[5] and personal communication with Crystal Nanoclay and Süd Chemie
Polypropylene	787	1191	€/tonne	Industry sources
Polyethylene	926	1401	€/tonne	Industry sources
GF/PP composite	1550	2000	€/tonne	[42]
Styrene	1060	1604	€/tonne	Industry sources
Maleic anhydride	694	1050	€/tonne	Industry sources
Electricity	18.3	-	€/GJ	[43]
Diesel	1.075	-	€/l	Price in March 2006 in NL
Incineration	100	-	€/tonne	[44]

Table 2.12: Price estimates for material and energy inputs in the life cycle of the products.

The costs for the conversion of plastic granules to the final product were estimated on the basis of information from a plastics processor (Landré Werkmetaal b.v., Vianen, The Netherlands) and are given in Table 2.13. It should be noted that these are very rough estimates. The uncertainty has, nevertheless, been neutralized to a large extent, because a comparative assessment was performed and the conventional polymers and the nanocomposites for each product were processed in the same way.

Production method	Costs (€/tonne)
Film extrusion	870
Blow molding	180
Injection molding	420

Table 2.13: Cost estimates of product forming methods.

In order to account for the price range given in Table 2.12, we calculated the production costs for four cases:

1. Low nanoclay price - Low price other material inputs
2. Low nanoclay price - High price other material inputs
3. High nanoclay price - Low price other material inputs
4. High nanoclay price - High price other material inputs

The price ranges of the input data could be accounted for by performing a cost analysis for these four cases.

	Life cycle costs conventional product (€ / functional unit)	Life cycle costs nanocomposite product (€ / functional unit)	Difference (%)
Case 1			
Packaging film	9.28	9.21	-0.8
Agricultural film	2877	1857	-35.5
Automotive panel	672.6	634	-6.1
Case 2			
Packaging film	11.4	11.1	-2.8
Agricultural film	4007	2448	-38.9
Automotive panel	700.5	655.3	-6.4
Case 3			
Packaging film	9.28	10.0	+7.9
Agricultural film	2877	2111	-26.6
Automotive panel	672.6	649	-3.5
Case 4			
Packaging film	11.4	11.9	+4.2
Agricultural film	4007	2702	-32.6
Automotive panel	700.5	672.5	-4.0

Table 2.14: Results life cycle costing.

2.3.4 Interpretation of the results

Table 2.14 shows that, in the cases with high nanoclay costs, the life cycle costs of nanocomposite packaging film are higher than those of conventional packaging film. In contrast, the life cycle costs of the nanocomposite agricultural film and automotive panels are consistently lower than those of the conventional products. The differences are largest between the nanocomposite and the conventional agricultural film. This can be explained by the fact that weight reduction was highest for the nanocomposite agricultural film.

Although the weight reduction was only 1.25% for the automotive panels, the nanocomposites have lower life cycle costs due to the relatively high costs of the PP-glass fiber composite (= conventional material).

Nanocomposite packaging film has higher life cycle costs in Cases 3 and 4 because its production requires many more production steps and material inputs than the conventional packaging film, which consists only of neat polypropylene. The 9% weight reduction could not compensate for this. A reduction of the nanoclay cost could, however, make the nanocomposite competitive with conventional packaging film in all cases. Table 2.15 shows the required nanoclay cost reduction. In the worst-case scenario, the nanoclay price must be lowered by 51%, if the initial price level is €10,000/tonne. This means that the nanoclay price can be at most €4900/tonne. In conclusion, all nanocomposite applications (packaging film, agricultural film, and automotive panels) are economically viable at a maximum nanoclay price of around €5000/tonne. At this price, the use of nanoclay in agricultural film offers very considerable cost savings.

	Nanoclay price (€/tonne)	Required reduction in nanoclay price
Case 1	4400	0 %
Case 2	4400	0 %
Case 3	10000	50.9 %
Case 4	10000	33.6 %

Table 2.15: Required nanoclay price reduction to make nanocomposite packaging film competitive.

2.4 Conclusions

The production of nanoclays and their incorporation in nanocomposites have an impact on the environment that may be compensated for if the weight reduction resulting from the use of nanocomposites is large enough. When a polypropylene nanocomposite is used for agricultural film, for example, there are clear environmental benefits due to the high estimated weight reduction. The use of a nanocomposite for packaging film and automotive panels, however, has no obvious environmental benefit.

From an economic point of view, the use of a nanocomposite in packaging film is advantageous if the nanoclay price is not higher than €5000/tonne. Depending on which material and energy prices are assumed, the life cycle costs can be reduced by 26-39%

when a polypropylene nanocomposite is used for agricultural film. We estimated the economic advantage of using nanocomposites in automotive applications to be 4-6%.

Based on the results of this study, we can conclude that the use of nanocomposite polypropylene *can* have clear environmental advantages over conventional material in certain circumstances. These advantages are mainly caused by a reduction in the amount of material needed, which depends on material properties like the Young modulus and tensile strength. We found, for example, a high increase in these properties compared to those of LDPE, which explains the large reduction in material. There were only small improvements (12% improvement in tensile strength) compared to neat polypropylene. Compared to glass fiber-reinforced polypropylene, the only improvement was reduced density. The Young modulus was even worse.

The use of polypropylene nanocomposites, therefore, only has advantages when it replaces polymers with less favorable material properties, e.g., LDPE.

It should, however, be stated that there are no disadvantages in using nanocomposites. In general, the nanocomposites do not have a higher environmental impact than conventional products. Moreover, they show some economic benefits when used in agricultural film and automotive panels and definite environmental benefits in the case of agricultural film. One exception to the use of nanocomposites may be the toxic effects of free nanoparticles: more research is required on this topic (see also Chapter 4). Provided the potential release of free nanoparticles from polymer nanocomposites can be excluded as source of concern for human health and the environment, the outcomes of the three PP nanocomposite cases clearly support further polymer research and technology development.

Acknowledgements

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CHAPTER 3

Influence of using nanoobjects as filler on functionality based energy use of nanocomposites

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Abstract

The goal of our study was to investigate the potential benefits of reinforcing polymer matrices with nanoobjects for structural applications by looking at both the mechanical properties and environmental impacts. For determining the mechanical properties we applied the material indices defined by Ashby for stiffness and strength. For the calculation of environmental impacts we applied the life cycle assessment methodology, focusing on non-renewable energy use (NREU). NREU has shown to be a good indicator also for other environmental impacts. We then divided the NREU by the appropriate Ashby index to obtain the ‘functionality based NREU’.

We studied twenty-three different nanocomposites, based on thermoplastic and thermosetting polymer matrices and organophilic montmorillonite, silica, carbon nanotubes (singlewalled and multiwalled) and calcium carbonate as filler. For seventeen of these, we saw a decrease of the functionality based NREU with increasing filler content. We draw the conclusion that the use of nanoobjects as filler can have benefits from both an environmental point of view and with respect to mechanical properties.

3.1 Introduction

The mechanical properties of polymers can be improved by adding fillers. A wide range of fillers has been available for years, including glass fiber, carbon black and natural fiber. Fillers with at least one dimension in the order of 1-100 nm are referred to as nanoobjects (comprising nanoparticles, that are nanoscale at 3 external dimensions; nanofibers, that are nanoscale in 2 external dimensions; and nanoplates, that are nanoscale on 1 external dimension). Examples are layered silicates (nanoplate), carbon nanotubes (nanofiber) and silica (nanoparticle). The use of nanoobjects for reinforcement of polymers is a new technology which faces high expectations since it has shown to improve the mechanical properties significantly. A very common layered silicate nanoobject is montmorillonite. Polymers blended with montmorillonite have improved mechanical and thermal properties, gas permeability resistance and fire retardancy [1].

The mechanical properties are an important factor for material choice in a specific application. Other important factors are other material properties (e.g. impact strength, sensitivity to water and other compounds and antistatic properties), the costs of the material and health and safety issues. However, with growing emphasis on sustainable development, the environmental performance of a material becomes increasingly important. Bio-based polymers are rapidly emerging on the market, because they are expected to have less impact on the environment by not using a petrochemical feedstock. Some of these polymers, however, lack the performance of many petrochemical polymers. The use of nanoscale fillers could solve this problem by improving the mechanical properties. The use of nanoobjects to reinforce plastics is referred to as nanotechnology and can improve the mechanical properties of both bio-based and petrochemical polymers. The improved mechanical properties could allow a reduction in the amount of material needed for an application (such as car panels or packaging film), as was shown previously [2]. If improved properties allow a reduction in material use, this might lead to a reduction in environmental impacts. However, the production and waste management of the nanoobjects could be accompanied by additional environmental impacts. It would therefore be very useful to have an indicator that addresses both the environmental performance of a material and its mechanical properties. In this study, we present and apply such an indicator: the ‘functionality based environmental impact’ focusing on non-renewable energy use. Life cycle assessment (LCA) is a methodology to assess the environmental impacts of a product throughout its life cycle [3]. It is therefore a good tool for assessing the environmental performance of a material. For the assessment of mechanical properties, we will use the material indices developed by Ashby [4] for stiffness and strength (see Section 3.2.1).

The method will be used to assess the potential benefits of using nanoobjects as filler in polymers compared to unfilled (neat) polymers or conventionally filled polymers. To this end, the non-renewable energy use for making the nanoobjects needs to be determined as well. In this paper we will discuss this for organophilic montmorillonite, silica and carbon nanotubes, based on published data and own estimates (Section 3.2.2). Next, we will determine the non-renewable energy use and mechanical properties of twenty-three different nanocomposites (based on both petrochemical and bio-based thermoplastics and thermosets). As nanoscale fillers we use organophilic montmorillonite, silica, carbon nanotubes (singlewalled and multiwalled) and calcium carbonate (CaCO_3). An overview of the nanocomposites studied in this paper is given in Table 3.1. The choice of these nanocomposites aims to cover the most important polymers (based on global production volumes) and is also determined by the availability of suitable studies on both production methods and mechanical properties. For all nanocomposites, the functionality based environmental impact is determined for different loads (including zero load) of filler. For PP-MMT, PHB-MMT and NR-MMT, a comparison with conventionally filled material is made as well, as can be seen from Table 3.1.

Nanocomposite-thermoplastic (petrochemical)	Abbreviation	Application^a
Nylon 6-montmorillonite	Nylon 6-MMT	Panel
Nylon 66-montmorillonite	Nylon 66-MMT	Panel
Polycarbonate-montmorillonite	PC-MMT	Panel
Poly(ϵ -caprolactone)- montmorillonite	PCL-MMT	Panel
Low-density polyethylene-montmorillonite	LDPE-MMT	Panel
Linear low-density polyethylene-montmorillonite	LLDPE-MMT	Panel
High-density polyethylene-montmorillonite	HDPE-MMT	Panel
Cross-linked low-density polyethylene montmorillonite	XLDPE-MMT	Panel
Polyethylene terephthalate-montmorillonite	PET-MMT	Panel
Poly (methyl methacrylate)-multiwalled carbon nanotubes	PMMA-MWNT	Panel
Polypropylene-montmorillonite	PP-MMT	Panel
Polystyrene-singlewalled carbon nanotubes	PS-SWNT	Panel
Poly(trimethylene terephthalate)-montmorillonite	PTT-MMT	Panel
Polyurethane-montmorillonite	PU-MMT	Panel
Polyvinyl chloride-montmorillonite	PVC-MMT	Tie
Polyvinyl chloride-calcium carbonate	PVC-CaCO ₃	Tie
Nanocomposite-thermoplastic (bio-based)		
Poly(hydroxybutyrate)-montmorillonite	PHB-MMT	Panel
Poly(lactic acid-pyrogenic silica	PLA-Si	Panel
Poly(lactic acid)-montmorillonite	PLA-MMT	Panel
Thermoplastic starch-montmorillonite	TPS-MMT	Panel
Nanocomposite-thermosets (petrochemical)		
Sulfonated ethylene-propylene-norbornene terpolymer-single walled carbon nanotubes	EPDM-SWNT	Tie
Epoxy- silica sol	Ep-Si	Panel
Nanocomposite-thermosets (bio-based)		
Natural rubber-montmorillonite	NR-MMT	Tie
Conventionally filled material		
Polypropylene-glass fiber	PP-GF	Panel
Poly(hydroxybutyrate)- sugarcane bagasse	PHB-BGS	Panel
Natural rubber-carbon black	NR-CB	Tie

Table 3.1: Composites studied in this paper.

^a See Section 3.2.1

In Section 3.2, the methodology of this study is explained (3.2.1), together with an inventory analysis and impact assessments for organophilic montmorillonite, silica and carbon nanotubes (3.2.2). In Section 3.3 the results are presented and they are discussed in Section 3.4. We present our conclusions in Section 3.5.

3.2 Methodology

3.2.1 Approach

For the assessment of the environmental impacts, we used the LCA methodology, as it has been standardized by the International Standards Organization (goal definition and scoping, inventory analysis, impacts assessment, life cycle interpretation) [5]. We determined the environmental performance on a cradle-to-grave basis. This means that we took into account all stages from raw materials extraction to waste management. We assume that nanocomposites are burned in a municipal waste incinerator and that for each gigajoule of waste 0.106 gigajoule of electricity and 0.223 gigajoule of heat is regained¹⁰ [6, 7]. The use phase is assumed to be stationary, which means that no extra energy use or material use is assigned to it. As a proxy for environmental impacts we studied non-renewable energy use (NREU) [8]. NREU has proven to be a good indicator also for other environmental impacts (such as global warming, acidification and ozone layer depletion) [9]. (It does not, however, include any information on health and safety issues, which is very important for nanomaterials! This requires separate research.)

For the determination of the mechanical properties, we used the material indices, as defined by Ashby [4]. Ashby developed a generic approach in order to determine the performance of a material in a given function. The performance of the material is expressed by Ashby's material index (MI), which is a function of material properties such as the Young modulus (E), tensile strength (σ_f) and density (ρ). Ashby developed equations for MI for different functional requirements, such as strength or stiffness¹¹. The larger the value for MI is, the better the mechanical properties of the product under consideration are and the less material is needed for a certain function. The material indices developed by Ashby are based on design that is 'stiffness-limited', 'strength-limited', 'vibration-limited', 'damage-tolerant', 'electro-mechanical' or 'thermal and thermo-mechanical'. Within each category, the appropriate function and constraints are

¹⁰ Although not all municipal waste incinerators use combined heat and power generation, we assume this type as average values for Europe.

¹¹ Apart from strength and stiffness, other important mechanical properties could be barrier properties and UV resistance. We limit ourselves to strength and stiffness because these properties are important for most applications of nanocomposites. Barrier properties are primarily important for packaging materials, while UV resistance is particularly needed for outdoor applications.

chosen (functions could be e.g. ‘tie’, ‘shaft’, ‘beam’, ‘column’, ‘panel’ or ‘plate’; constraints could be e.g. required specification of dimensions).

For the (nano-)composites with ‘panel’ as an application (Table 3.1) we assume a flat plate, which is stiffness-limited and loaded by bending. For such a plate (called ‘panel’), Ashby defined the following material index [eq. 1]:

$$MI_{\text{panel}} = E^{1/3}/\rho \quad (\text{unit: MPa}^{1/3} \cdot \text{dm}^3 \cdot \text{kg}^{-1}) \quad (1)$$

For the (nano-)composites with ‘tie’ as an application (Table 3.1), we assume that it will be applied in products that are strength limited, such as films (the material should not break or tear apart). The stress applied to the material, trying to break it during use, is ‘tie’. Ashby defined the following material index for such an application [eq. 2]:

$$MI_{\text{tie}} = \sigma_f/\rho \quad (\text{unit: MPa} \cdot \text{dm}^3 \cdot \text{kg}^{-1}) \quad (2)$$

The functionality based environmental impacts are now calculated as [eq. 3]:

$$\text{Functionality based environmental impact} = \frac{\text{Environmental impact}}{\text{Material index}} \quad (3)$$

In case the ‘Material index’ is MI_{panel} the unit is: $\text{MJ} \cdot \text{kg} \cdot \text{MPa}^{-1/3} \cdot \text{dm}^{-3}$

In case the ‘Material index’ is MI_{tie} the unit is: $\text{MJ} \cdot \text{kg} \cdot \text{MPa}^{-1} \cdot \text{dm}^{-3}$

To determine the environmental impacts of common polymers such as EPDM or polypropylene, data are readily available via databases such as Ecoinvent [10] and PlasticsEurope [11]. For other materials, such as poly(ϵ -caprolactone) or tetraethoxysilane and Jeffamine D2000 (used in the production of epoxy-silica nanocomposite), we had to derive the impacts ourselves. This was done by analyzing the production of those materials (making use of chemical encyclopedias [12-14]) and estimating material and energy requirements. Then we used the Ecoinvent databases (available in SimaPro [15]) for completing the inventory analysis which is the basis of the impact assessment.

3.2.2 Environmental assessment of nanoobjects

Since the environmental impacts of the nanoobjects used as filler may contribute significantly to the environmental impacts of nanocomposites, we gathered information regarding their production and environmental impacts. For organophilic montmorillonite

and carbon nanotubes, published studies exist on an environmental assessment. We will discuss these studies (Section 3.2.2.1 and 3.2.2.3.). For silica, environmental impacts have not yet been studied and will be estimated in this paper (Section 3.2.2.2). The environmental assessments will focus on NREU and impact on climate change¹².

3.2.2.1 Impact assessment of organophilic montmorillonite

Two studies were found in which the production of organophilic montmorillonite is studied. In Roes et al. [2] life cycle inventory data are presented and in Joshi [17] environmental impacts are presented. Table 3.2 shows the NREU and contribution to climate change as obtained/calculated from each of these studies.

Study	NREU (MJ/kg)	Climate change (kg CO ₂ -eq/kg)
Roes et al. (2007)	69.7	3.55
Joshi (2008)	40.1	1.52

Table 3.2: Environmental impacts of organophilic montmorillonite.

From Table 3.2 it appears that the environmental impacts in the study by Joshi (2008) are lower than in the study by Roes *et al.* (2007). Since both studies are based on personal communication with a manufacturer and the data sources of Joshi (2008) cannot, as such, be traced back, we use own values from earlier research (from Roes *et al.* 2007) in the calculations in this study. However, the uncertainty will be addressed in the uncertainty analysis in Section 3.4.3.

3.2.2.2 Impact assessment of silica

For silica, no published studies on environmental impacts were found. Therefore we will present both the inventory data and the environmental impacts of silica. Nanoscale silica (SiO₂) is manufactured at industrial scale in four types: silica sol (i.e. colloidal silica), silica gel, precipitated silica and pyrogenic silica. These types differ in the way the particles are agglomerated. Figure 3.1 shows the typical structures of the four types of silica. Using data from a report by the European Commission [18] and the stoichiometry of the reactions to produce the silica an inventory analysis was made from

¹² Impact on climate change is defined as the Global Warming Potential in the next 100 years (GWP₁₀₀). The methodology is described by the Intergovernmental Panel on Climate Change (IPCC) [16].

which environmental impacts were calculated. Table 3.3 and Table 3.4 show the material and energy requirements for the production of silica sol, silica gel, precipitated silica and pyrogenic silica. The material requirements for silica sol, silica gel and precipitated silica are essentially identical. Differences concern only the manufacturing process but not the material requirements. Silica gel and precipitated silica, however, are sold as dry powder, while silica sol is sold as a suspension. Natural gas is used for drying of the silica gel and precipitated silica. For silica sol, natural gas is used to increase the concentration directly after manufacturing from 10% to 20%. According to the report by the European Commission [18], natural gas use for drying silica gel and precipitated silica is 15-24 MJ/kg¹³. Since no data are reported for silica sol, a producer was contacted [19], who estimated natural gas use to be 36 MJ/kg. Because silica sol is not completely dried, it is questionable whether energy use for silica sol is so much higher than for silica gel and precipitated silica. A calculation based on heat of evaporation of water (for increasing the concentration from 10% to 20% solids) yields 11 MJ/kg silica sol. Given this uncertainty, if the inventory data from Table 3.3 are used for any calculation, both values (11 MJ/kg and 36 MJ/kg) should be used to arrive at a 'best estimate' and a 'worst estimate' (see Table 3.4; the same holds for the value range for drying of silica gel and precipitated silica [15-24 MJ/kg] and the energy use for pyrogenic silica [15-18 MJ/kg]).

All processes yield more than one product (see Tables 3.3 and 3.4). We therefore applied the system expansion method [20], thereby assuming that the co-products would have been manufactured according to the dominating industrial processes. In Table 3.5, the environmental impacts are shown of the different silica types.

¹³ Also for pyrogenic silica natural gas is consumed. It is used for heating hydrogen gas and combustion air, for the evaporation of silicon tetrachloride, as well as for removing residual hydrochloride from the silica surface.

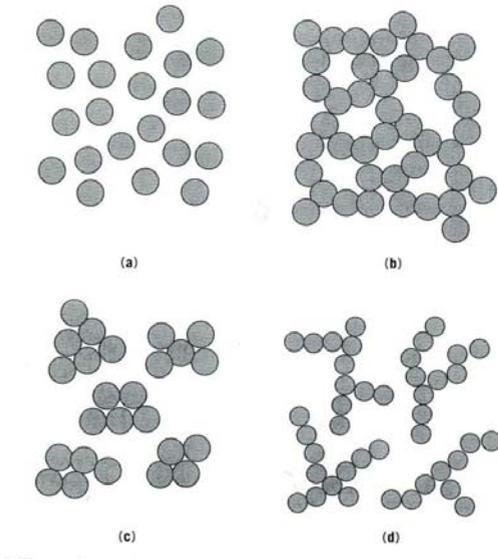


Figure 3.1: Different forms of commercially important amorphous silica: (a) sol, (b) gel, (c) precipitate, and (d) pyrogenic [21]. Reproduced with permission of John Wiley & Sons, Inc.

Input	Amount for silica gel and precipitated silica	Amount for silica sol	Unit
Sodium silicate	3.9	3.9	kg
Sulfuric acid	0.66	0.66	kg
Natural gas (for silica gel and precipitated silica)	15-24	11-36	MJ
Water	40	40	kg
Output	Amount	Amount	Unit
Silica gel / precipitated silica / silica sol	1	1	kg
Sodium sulphate	0.96	0.96	kg
Emissions to air	Amount	Amount	Unit
Particulates	0.0013	0.0013	kg
Emissions to water	Amount	Amount	Unit
Waste water	35	35	kg

Table 3.3: Material and energy requirements and emissions for the production of silica gel, precipitated silica and silica sol [18].

Input	Amount	Unit
Silicon tetrachloride	2.83	kg
Hydrogen	0.067	kg
Natural gas	15-18	MJ
Output	Amount	Unit
Pyrogenic silica	1	kg
Hydrochloric acid	2.43	kg
Emissions to air	Amount	Unit
Particulates	0.0003	kg
NO _x	0.0001	kg
Cl ₂	0.00005	kg
HCl	0.00001	kg
VOC	0.0003	kg
CO ₂	0.64	kg

Table 3.4: Material and energy requirements and emissions to air for the production of pyrogenic silica [18].

Silica type	NREU (MJ/kg)		Climate change (kg CO₂-eq/kg)	
	Low estimate	High estimate	Low estimate	High estimate
Silica sol	61.0	92.2	3.20	4.98
Silica gel	66.0	77.3	3.48	4.12
Precipitated silica	66.0	77.3	3.48	4.12
Pyrogenic silica	63.7	67.4	4.57	4.78

Table 3.5: Environmental impacts caused by the production of silica.

3.2.2.3 Impact assessment of carbon nanotubes

For the environmental assessment of carbon nanotubes, two studies have been published: Kushnir and Sandén (2008) [22] and Healy *et al.* (2008) [23]. These studies cover several production processes¹⁴ for singlewalled carbon nanotubes (SWNT) and multiwalled carbon nanotubes (MWNT) and are based on publicly available data and on information provided by manufacturers. The results in the two studies differ enormously, however. For example, regarding electricity use in the high pressure carbon monoxide process

¹⁴ Included processes are: Fluidized bed and floating catalyst chemical vapor deposition, high pressure carbon monoxide process, electric arc process, laser ablation process and solar furnace process.

(HiPco), Kushnir and Sandén have estimated 6 GJ_e/kg, whereas Healy et al. arrive at 145 GJ_e/kg. This reflects the high uncertainty in process data as available to researchers. In 2009, Bayer Material Science (BMS) AG (Leverkusen, Germany) announced to set up the industrial production of carbon nanotubes in a plant with a capacity of 3000 tonnes per year. The applied process is fluidized-bed chemical vapour deposition (for information, see: www.baytubes.com). Data for this process should best reflect large scale industrial practice. In order to obtain realistic process data of this process, the head of Bayer's Working Group Nanotechnology was contacted [24]. Unfortunately, due to strict confidentiality regulations it was not possible to disclose any information regarding the process in their factory. However, process data for the fluidized bed chemical vapour deposition (baseline case), published by Kushnir and Sandén, were confirmed to be a reasonable estimate for a large-scale plant (with small-scale plants having an energy use that can be up to 1000 times larger) [24]. These data hold for single-walled carbon nanotubes (SWNT), while BMS produces exclusively multi-walled carbon nanotubes (MWNT). The structure, production process and applications for SWNT and MWNT are totally different. According to personal communication with Bayer [24], the energy use of MWNT production is roughly 10% of the energy use of SWNT and it is in the worst case somewhere in the order of magnitude of the energy use of carbon black production. The energy use for SWNT and MWNT production as estimated on the basis of this information is listed in Table 3.6.

	Thermal energy (MJ _{th} /kg)	Electric energy (MJ _e /kg)	Source
SWNT	328	626	[22]
MWNT	32.8	62.6	[24]

Table 3.6: Energy use in the production of SWNT and MWNT.

The production of carbon black uses 9 MJ/kg natural gas and 79 MJ/kg oil (power use is not mentioned) [12]. This is 88 MJ final energy. The production of MWNT uses 95.4 MJ final energy. This roughly supports the data for MWNT as derived from Kushnir and Sandén and personal communication with Bayer [24]. The environmental impacts of SWNT and MWNT are listed in Table 3.7.

	NREU (MJ/kg)	Climate change (kg CO ₂ -eq/kg)
SWNT	2145	110
MWNT	215	11

Table 3.7: Environmental impacts caused by the production of carbon nanotubes.

3.3 Results

Non-renewable energy use (NREU) of the nanocomposites and unfilled or conventionally filled materials was determined with help of the Ecoinvent databases. The Ashby material indices were determined, based on the Young's modulus, the tensile strength and the density. From the analyses, it appeared that there was a large variation in mechanical properties as a consequence of the methods applied for nanocomposite preparation. These differences could be the result of, for example, the method of mixing the nanoscale filler and the polymer matrix (solvent casting or extrusion, different temperatures, different equipment), or the type of surfactant and/or compatibilizer used to enhance exfoliation of the filler in the matrix. However, in order to fully determine the potential benefits of using nanoobjects to reinforce polymers, we assume best available technology. Therefore, if different results were obtained with data applying different techniques, we present only the best case. But in order to get a better understanding of the possible reasons for differences, we present for one nanocomposite (LDPE-MMT) all results for various techniques and we explain the differences. The results are shown in Figures 3.3a-d and 3.4a-c. Note that the value ranges are quite different in Fig 3.3a and 3.3b-d and in 3.4b and 3.4a,c. The literature sources from which the data for the analyses were taken are listed in Table 3.8.

The results show that for PC-MMT, LLDPE-MMT, PTT-MMT, HDPE-MMT, TPS-MMT, Ep-Si, PCL-MMT, PU-MMT, XLDPE-MMT, LDPE-MMT, Nylon 66-MMT, PET-MMT, Nylon 6-MMT, PLA-Si, PMMA-MWNT¹⁵, NR-MMT, EPDM-SWNT and PVC-MMT, the functionality based NREU decreases with increasing filler content (this is a desirable outcome). It is reflected by a negative slope of the plots. PP-MMT has slightly higher functionality based NREU than PP-GF (see Fig. 3.3a). Also the PHB composites using a nanoobject (MMT) cause higher functionality based environmental impacts than the PHB composite using a natural fiber (BGS). Nanocomposites for which the functionality based NREU increases with increasing filler content (positive slope of the plot) are PP-MMT, PHB-MMT, PS-SWNT, PLA-MMT and PVC-CaCO₃ (no desirable outcome).

¹⁵ The slope of this line is negative, albeit minor.

Nanocomposite-thermoplastic (petrochemical)	Reference
Nylon 6-montmorillonite	[25]
Nylon 66-montmorillonite	[25]
Polycarbonate-montmorillonite	[26]
Poly(ϵ -caprolactone)- montmorillonite	[27]
Low-density polyethylene-montmorillonite	
- Na ⁺ , Cloisite B, Cloisite C, Cloisite 30B, Cloisite D	[28]
- Triclay	[29]
- Lauryl clay	[30]
- Triclay II	[31]
- Octadecylamine (ODA)	[32]
Linear low-density polyethylene-montmorillonite	[33]
High-density polyethylene-montmorillonite	[34]
Cross-linked low-density polyethylene montmorillonite	[35]
Polyethylene terephthalate-montmorillonite	[36]
Poly (methyl methacrylate)-multiwalled carbon nanotubes	[37]
Polypropylene-montmorillonite	estimate from [38] and [39]
Polystyrene-singlewalled carbon nanotubes	[40]
Poly(trimethylene terephthalate)-montmorillonite	[41]
Polyurethane-montmorillonite	[42]
Polyvinyl chloride-montmorillonite	[43]
Polyvinyl chloride-calcium carbonate	[44]
Nanocomposite-thermoplastic (bio-based)	
Poly(hydroxybutyrate)-montmorillonite	[45]
Polylactic acid-pyrogeic silica	[46]
Polylactic acid-montmorillonite	[47]
Thermoplastic starch-montmorillonite	[48]
Nanocomposite-thermosets (petrochemical)	
Sulfonated ethylene-propylene-norbornene terpolymer-singlewalled carbon nanotubes	[49]
Epoxy- silica sol	[50]
Nanocomposite-thermosets (bio-based)	
Natural rubber-montmorillonite	[51]
Conventionally filled material	
Polypropylene- glass fiber	[38, 52]
Poly(hydroxybutyrate)- sugar cane bagasse	[45]
Natural rubber-carbon black	[51]

Table 3.8: Data sources used in the assessment of mechanical properties.

As explained above (see equation 3), the functionality based environmental impact depends on the one hand on the environmental impact (NREU) and on the other hand on the Ashby material index (MI_{panel} , MI_{tie}). Only if the addition of a filler causes an increase in the material index that is larger than the increase in environmental impact, caused by the production of the nanoparticles and their dispersion in the polymer matrix, the functionality based environmental impact will decrease with increasing filler content. For functionality based NREU, this is the case for the nanocomposites that show a negative slope in Figures 3.3 and 3.4. For PP-MMT and PLA-MMT, PS-SWNT, the material index increases with increasing filler content, but the increase of NREU is larger, caused by the extra impacts of adding nanoobjects, resulting in an increasing functionality based NREU. Especially the use of carbon nanotubes in the PS-SWNT nanocomposites causes a large increase in NREU, due to the very high environmental impacts of carbon nanotube production (see Table 3.7). The reason that the PHB nanocomposite using MMT has increasing functionality based NREU (Figure 3.3a), is because on one hand there is a decrease in material properties and on the other hand the environmental impacts increase as a result of the production and adding of the nanoobjects.

Natural rubber filled with 10% nanoclay (i.e. organophilic MMT) causes lower functionality based environmental impacts than unfilled natural rubber (Figure 3.4a). If other fillers are used (carbon black or unmodified clay), there are no benefits at all. The reason is that NR-10MMT has a very high tensile strength (105 MPa) compared to the other samples. The negative values for functionality based NREU are caused by energy credits in the waste stage and by the fact that NREU of natural rubber is low, since it is a bio-based material.

PVC- CaCO_3 has a decreasing NREU (per kg) with increasing filler content, but the mechanical properties are bad and decrease faster than the NREU (per kg; see Figure 3.4c). The resulting functionality based NREU therefore increases.

The result for PVC-MMT is somewhat irregular; for small additions of a nanoscale filler, the functionality based NREU decreases, but starts increasing if more filler is used. This is caused by the fact that the use of MMT improves the tensile strength drastically already at low content (from 51 MPa for pure PVC to 62 MPa at 0.5% MMT), but if more filler is used, the tensile strength (and the material index) starts decreasing. A similar pattern is observed for PMMA-MWNT.

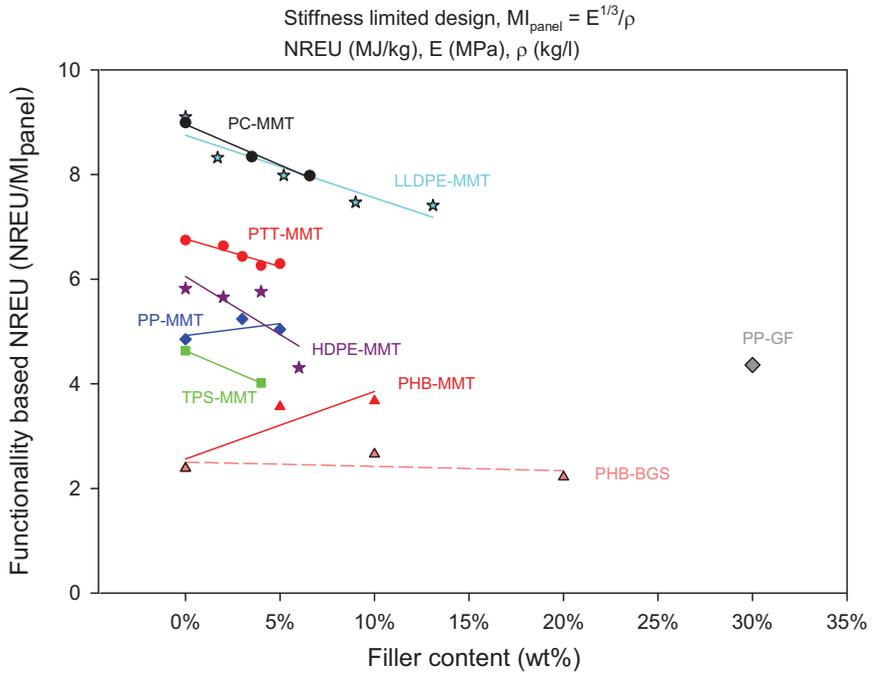


Figure 3.3a: Functionality based NREU of panels with stiffness-limited design.

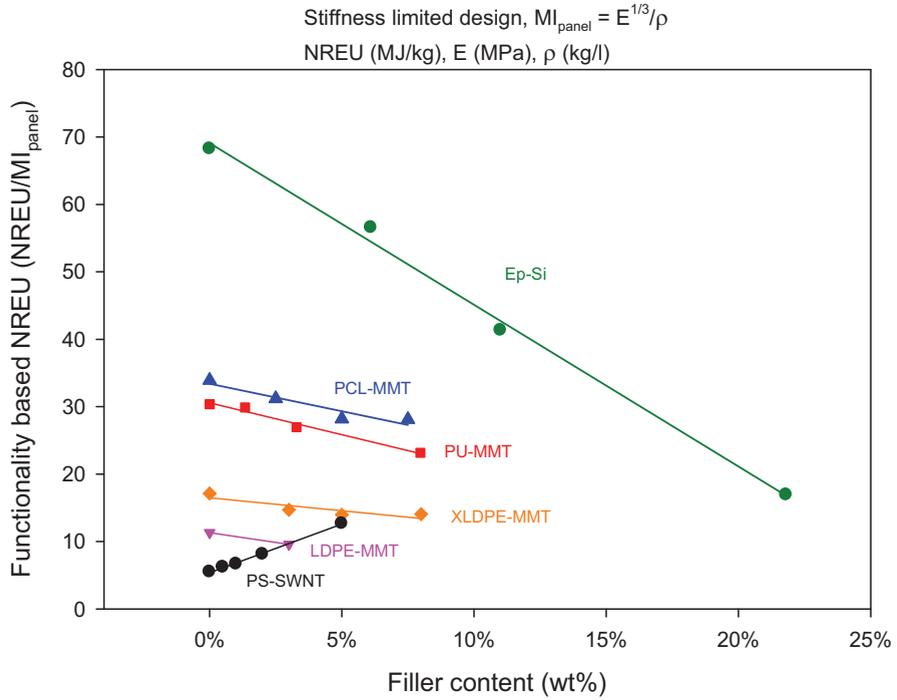


Figure 3.3b: Functionality based NREU of panels with stiffness-limited design (continued).

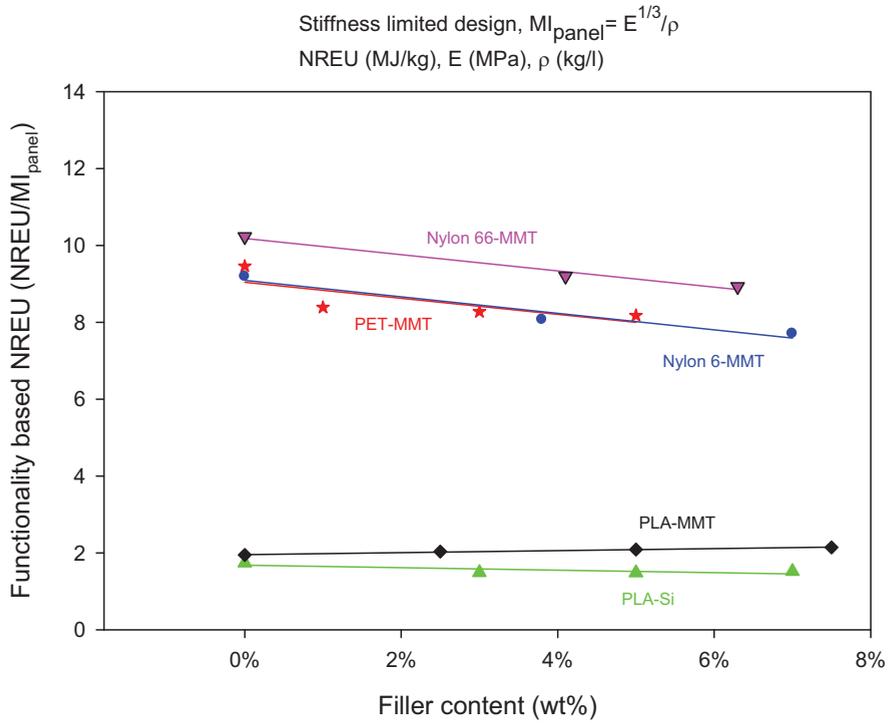


Figure 3.3c: Functionality based NREU of panels with stiffness-limited design (continued).

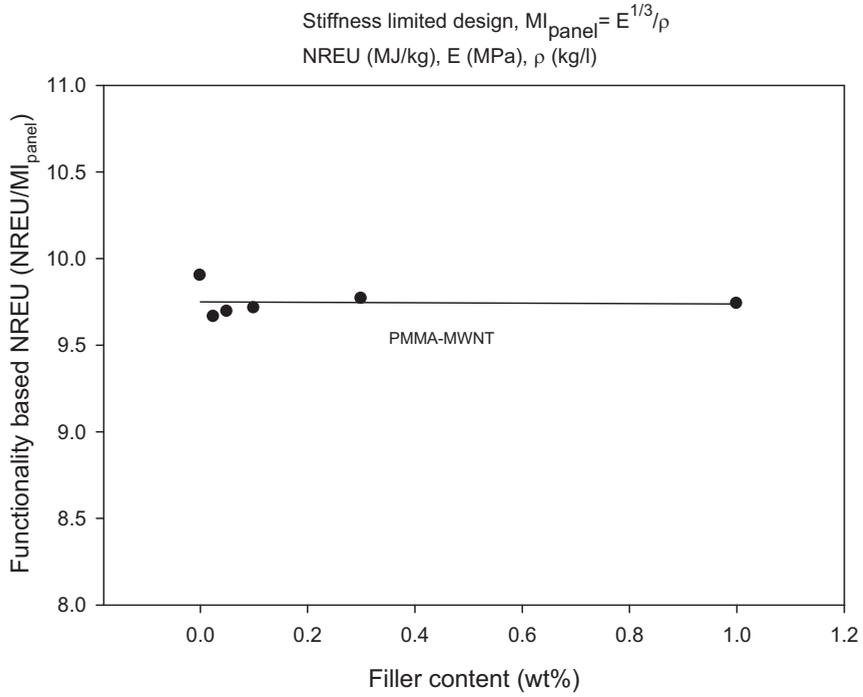


Figure 3.3d: Functionality based NREU of panels with stiffness-limited design (continued).

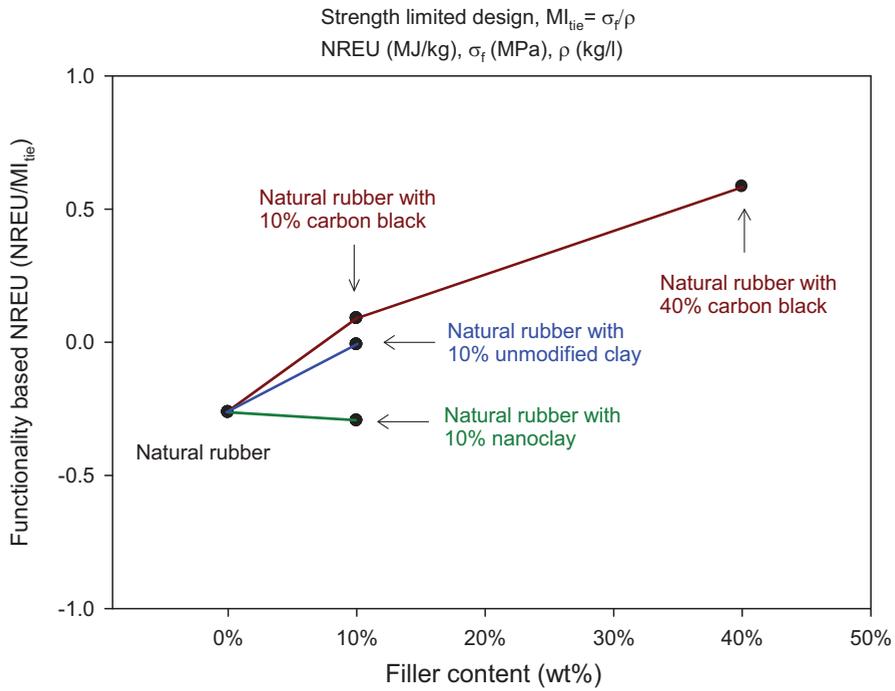


Figure 3.4a: Functionality based NREU of a natural rubber based tie with strength-limited design.

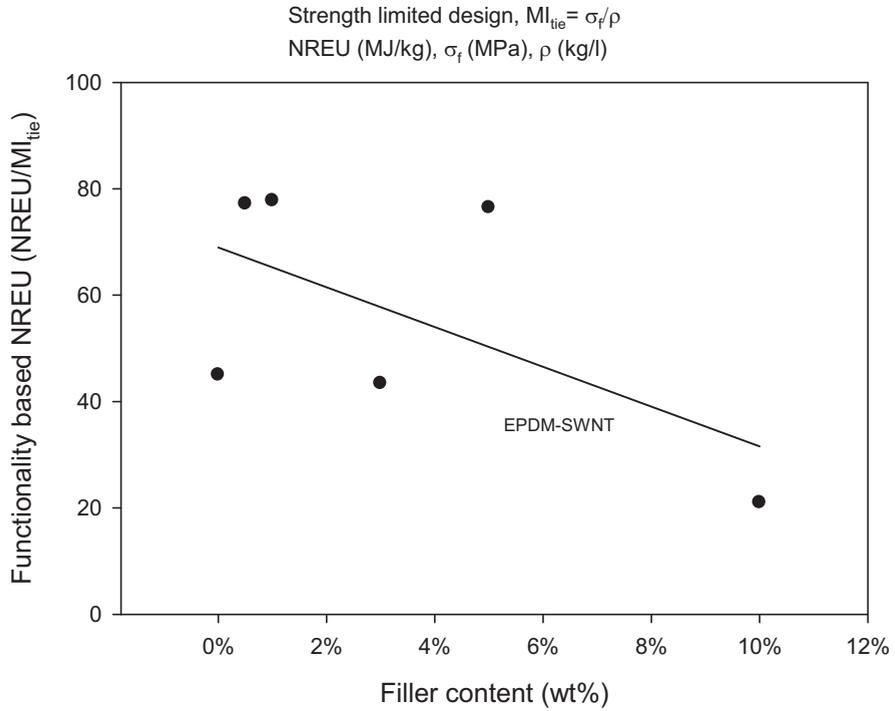


Figure 3.4b: Functionality based NREU of an EPDM-SWNT tie with strength-limited design.

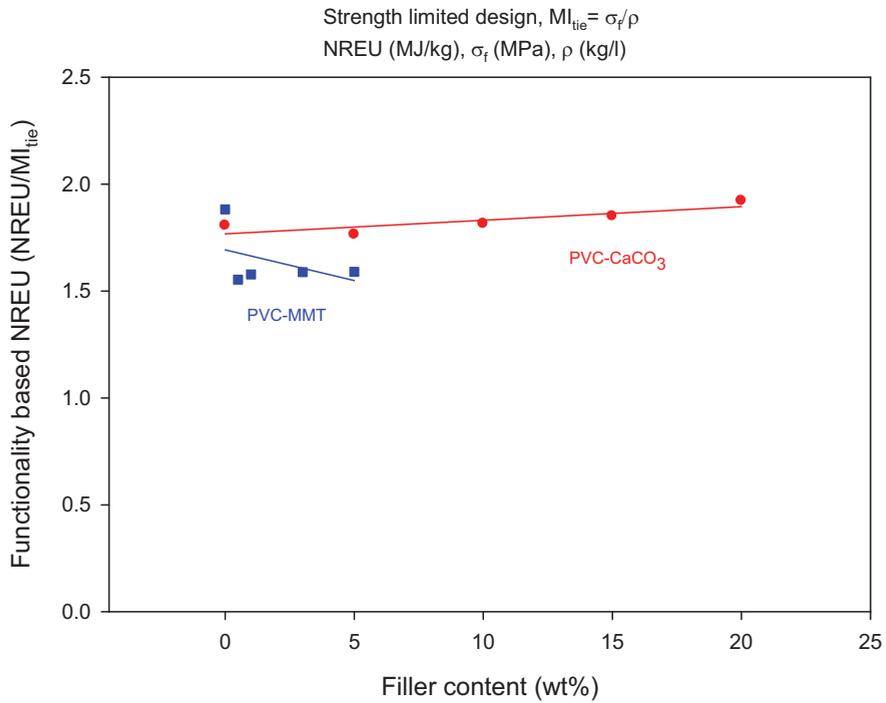


Figure 3.4c: Functionality based NREU of a PVC-MMT and PVC-CaCO₃ tie with strength-limited design.

3.4 Discussion

3.4.1 Analysis of factors influencing mechanical properties

In order to optimize the mechanical properties of nanocomposites, it is important that the particles and the polymer matrix are optimally mixed and bound to each other. Often, the fabrication of polymer nanocomposites is hindered by the tendency of the nanoobjects to form agglomerates. The presence of agglomerates in a polymer nanocomposite can negate the advantages of the nanoobject filler because: a) under load there may be slippage within the agglomerate, b) it reduces the surface area for the interaction between the nanoobjects and the polymer and c) it can initiate fracture at the agglomerate sites [53]. To prevent agglomeration, several methods can be applied. West and Malhotra (2006) report a new technique applying ultrasonic cavitation using a high intensity ultrasonic processor. The ultrasonic probe creates pressure waves, which destroy agglomerates. Another way to achieve optimal dispersion, is by treating the surface of the nanoobjects. This can be done in various ways, which are linked to the physical and chemical properties of both the nanoobject and the polymer. Different conditions give different results (also for the functionality based environmental impacts), so it is important to create optimal conditions. We will discuss the influence of various conditions on the basis of LDPE-MMT as an example. This nanocomposite uses montmorillonite as filler. Montmorillonite is a type of clay of which the particles are plate-shaped, which form layers. An example of the layered structure is shown in Figure 3.5. The gap between the layers is called the interlayer or the gallery. The distance between the clay layers is defined as the interlayer spacing, basal spacing or d-spacing. The galleries are occupied by cations such as Na^+ .

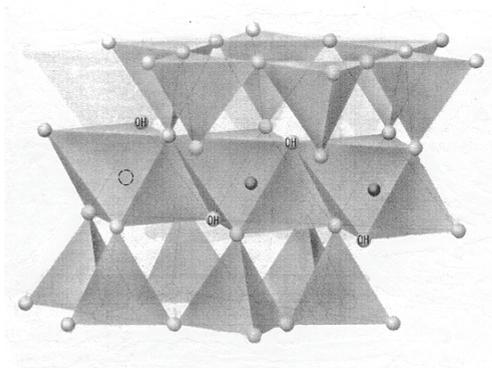


Figure 3.5: The layered structure of montmorillonite [54]. Reproduced with permission of Nanocor, Inc.

The material properties of a nanocomposite are maximally improved when the layers are randomly distributed in the polymer matrix. This means that all individual layers are separated and there is maximal contact with the matrix. This is called exfoliation or delamination. In some cases, the clay is only partly separated and several layers still stick together, but with the polymer in between them. This is called intercalation. Achievement of full exfoliation is difficult because montmorillonite is hydrophilic. Most polymers, especially thermoplastics, are mainly hydrophobic. The surface of the clay can be modified in order to decrease the surface tension. The surface can be modified by surfactants that exchange the positively charged inorganic ions in the interlayer distance for positively charged organic ions. These surfactants make the surface of the clay more organophilic. They also increase the interlayer distance. As a consequence the clay is better miscible with the polymer matrix. If the surfactant molecules are not sufficient for full exfoliation, a compatibilizer can be added as well. This is a molecule which is compatible with the surfactant and the polymer matrix. The most widely applied compatibilizer is maleic anhydride grafted polymer [33].

In the example of LDPE-MMT nanocomposite, various surfactants and/or compatibilizers are used, leading to different results (for references, see Table 3.8). An overview is given in Table 3.9. The results for functionality based NREU are shown in Figure 3.6.

Name of filler¹⁶	Description
MMT-Na ⁺	Untreated clay
MMT-Cloisite B	MMT-Na ⁺ which is ion exchanged with octadecylammonium chloride
MMT-Cloisite C	MMT-Cloisite B which is ion exchanged with octadecylamine
MMT-Cloisite 30B	MMT treated with methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (MT2EtOH), having hydroxyl groups
MMT-Cloisite D	MMT-Cloisite 30B treated with octadecylamine
MMT-Triclay	MMT that is oligomerically modified by a terpolymer of lauryl acrylate, styrene and vinylbenzyl chloride
MMT-Lauryl Clay	MMT that is oligomerically modified by a copolymer of lauryl acrylate and vinylbenzyl chloride
MMT-ODA	Octadecyl amine modified Nanomer I30P from Nanocor (USA). Maleic anhydride grafted polyethylene is used as a compatibilizer

Table 3.9: Descriptions of the various filler types used in LDPE nanocomposite.

¹⁶ Only in MMT-ODA a compatibilizer is used. In all other fillers only surfactants are used.

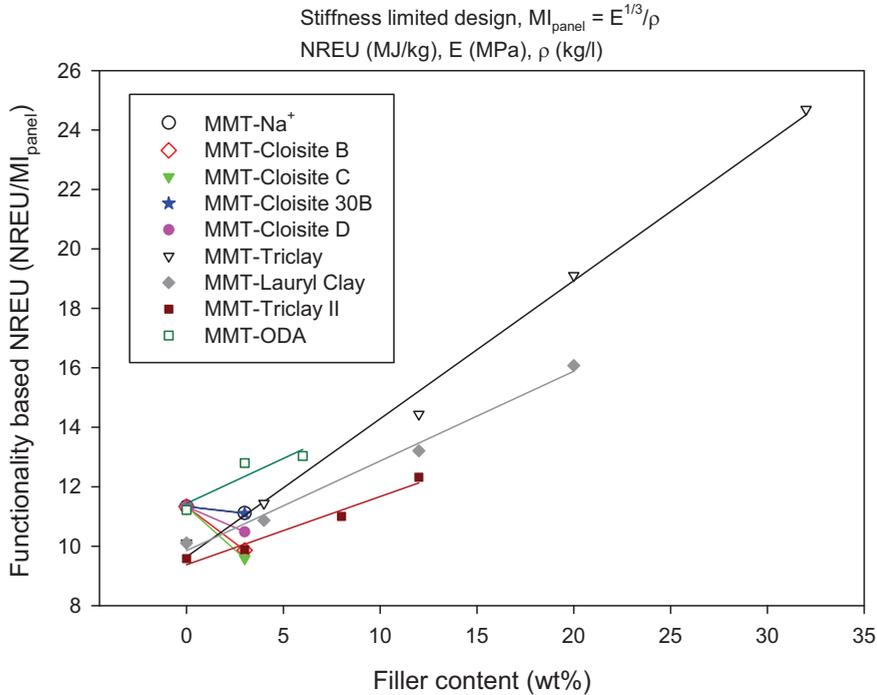


Figure 3.6: Functionality based NREU of LDPE-MMT panels with stiffness-limited design¹⁷ (MMT-Na⁺ is hidden beneath MMT-Cloisite 30B).

Figure 3.6 shows that the starting point for neat LDPE (0% filler) is different for some of the samples. Although the NREU can be assumed to be identical for all unfilled LDPE samples, there is some variation in Young's modulus as it is reported by the sources from which the mechanical properties are taken (measuring mechanical properties is a very sensitive process that can give different results when different equipment is used and for different samples, even if it is the same material). This results in different material indices and thus different functionality based NREU. Nevertheless, the figure shows that all

¹⁷ The choice of stiffness limited design ('Panel') for LDPE nanocomposites could be questioned, since LDPE is primarily used for films and sheets [55], for which the design would normally be strength limited ('Tie'). However, LDPE could also be used for applications which should be stiff. In fact, in the studied articles on LDPE nanocomposites, the Young modulus (indicating stiffness) was reported for all LDPE-MMT alternatives, while tensile strength (indicating strength) was reported for only a limited number of alternatives, making it impossible to perform an assessment for 'Tie' for all LDPE nanocomposites.

Cloisite nanocomposites and a nanocomposite with untreated clay (MMT-Na⁺) have a decrease in functionality based NREU with increasing filler content. For MMT-Triclay, MMT-Lauryl Clay and MMT-ODA the functionality based NREU increases.

The negative results for MMT-Triclay, MMT-Lauryl clay and MMT-ODA are a result of a strong increase of NREU with increasing filler content, while the material index remains more or less equal (MMT-Triclay II) or decreases (MMT-Triclay, -Lauryl clay and -ODA). The increase in NREU is a result of extra impacts of the incorporation of nanoobjects compared to unfilled LDPE. The fact that the material indices of LDPE-MMT-Triclay (and II) and LDPE-MMT-Lauryl clay do not improve with increasing filler content could be a result of the fact that the oligomeric molecules by which the clay is modified are too large to penetrate into the interlayer spacing, which makes exfoliation difficult.

When ODA is used for treatment of MMT, the Young's modulus of the nanocomposite increases slightly, but the increase in density is stronger, resulting in a decrease of the material index (see Eq. 1). As a consequence, the functionality based NREU increases with rising filler content.

Type of LDPE nanocomposite	Filler content (wt%)	NREU (MJ/kg)	MI _{panel} (MPa ^{1/3} .l.kg ⁻¹)	Funct based NREU (MJ.kg.MPa ^{-1/3} .l ⁻¹)
Unfilled	0	56.5	4.98	11.3
MMT-Na ⁺	3	55.0	4.95	11.1
MMT-Cloisite B	3	57.1	5.79	9.86
MMT-Cloisite C	3	56.9	5.93	9.58
MMT-Cloisite 30B	3	57.1	5.14	11.1
MMT-Cloisite D	3	56.9	5.42	10.5

Table 3.10: Results for neat LDPE, LDPE with untreated clay and LDPE with Cloisite clays.

For the Cloisite clays, the results are better. Table 3.10 gives details of the results. It shows that the material indices of all Cloisite nanocomposites improve compared to unfilled LDPE. Only for LDPE with untreated clay there is no improvement. However, for all Cloisite nanocomposites, the NREU in MJ per kg is higher compared to neat LDPE while for LDPE with untreated clay (MMT-Na⁺) it is slightly lower.

The best results are for LDPE-MMT-Cloisite C followed by LDPE-MMT-Cloisite B. All Cloisite clays use surfactants to make the clay more hydrophobic and/or to increase the interlayer distance. The surfactants occupy the space between the platelets and due to their large size the distance between the platelets is increased. The large alkyl tails make

the clay more hydrophobic. In the case of Cloisite B, the interlayer spacing is increased due to the ion exchange of Na^+ with octadecylammonium chloride. In Cloisite C the interlayer spacing is increased even more due to extra ion exchange with octadecylamine. This is shown in Figure 3.7. This increase in interlayer distance results in good exfoliation and thus in an improvement of the mechanical properties. The reason for the slightly smaller material indices of LDPE-MMT-Cloisite 30B and LDPE-MMT-Cloisite D could be the presence of hydroxyethyl groups, which are hydrophilic and therefore less mixable with the hydrophobic polymer matrix.

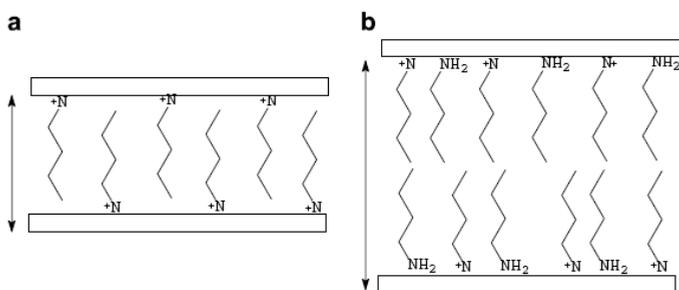


Figure 3.7: Schematic structure of Cloisite B (a) and Cloisite C (b) [28]. Reproduced with permission of Elsevier Ltd.

3.4.2 Extrusion

Polymers that are blended with color pigments or additives are often sold on the market as ‘masterbatches’. Such a masterbatch contains a high concentration of the additive and can be diluted or mixed with pure polymers and/or other masterbatches for further processing. Nanocomposites have not yet been produced on a large scale and we are not aware of commercial masterbatches for nanocomposites. However, masterbatches have been used in the laboratory scale production of PP-MMT and LDPE-MMT-ODA, both of which use a compatibilizer (maleic anhydride) to graft the polymer matrix. The masterbatches consist of the grafted polymer, some neat polymer resin and nanoclay. Prior to product forming, the masterbatches were diluted and subsequently extruded. The use of a masterbatch thus involves an extra extrusion step, i.e. one to produce the masterbatch and one for dilution and extrusion of the product. This extra extrusion step may also be needed if no grafted polymer is used, i.e. if the polymer resin is directly mixed with the nanoobject. Especially in the laboratory production of nanocomposites an extra extrusion is needed to achieve optimal mixing of the polymer matrix with the

nanoobject. However, if a large extruder is used, the mixing can be done in one go together with product forming. Although this study is to a large extent based on laboratory data and lab-scale technology, we try to extrapolate our assumptions to large-scale industrial practice if possible. We therefore base our calculations on one extrusion for both mixing of the nanoobject with the polymer matrix and product forming.

In case we would assume two extrusions, the results change slightly. For the unfilled polymer only one extrusion is needed, i.e. for product forming. As soon as a filler is used (which represents the much more common case), an extra extrusion for mixing is needed, which increases the environmental impacts and thus the functionality based NREU. Although for most results presented in this paper the difference is not significant (an increase in filler content still causes an overall decrease in functionality based NREU), we observed a change in case of the MMT-Cloisite filled LDPE nanocomposites. If a second extrusion were assumed, the addition of a nanoobject would not be beneficial anymore for LDPE-MMT- Na^+ , LDPE-MMT-Cloisite 30B and LDPE-MMT-Cloisite D, as is shown in Figure 3.8.

The NREU for extrusion is assumed to be 7.0 MJ/kg [56, 57]. For the LDPE nanocomposites, the MI_{panel} is between 5 and 6 $\text{MPa}^{1/3} \cdot \text{dm}^3 \cdot \text{kg}^{-1}$. This means that an extra extrusion adds 1.2-1.4 $\text{MJ} \cdot \text{kg} \cdot \text{MPa}^{-1/3} \cdot \text{dm}^{-3}$ to the functionality based NREU. This difference is significant, given the value range of the results. In other cases, the MI_{panel} is higher (sometimes $> 10 \text{ MPa}^{1/3} \cdot \text{dm}^3 \cdot \text{kg}^{-1}$) and the resulting contribution of an extra extrusion becomes very small and does not influence the overall results (the slope of the regression line remains negative).

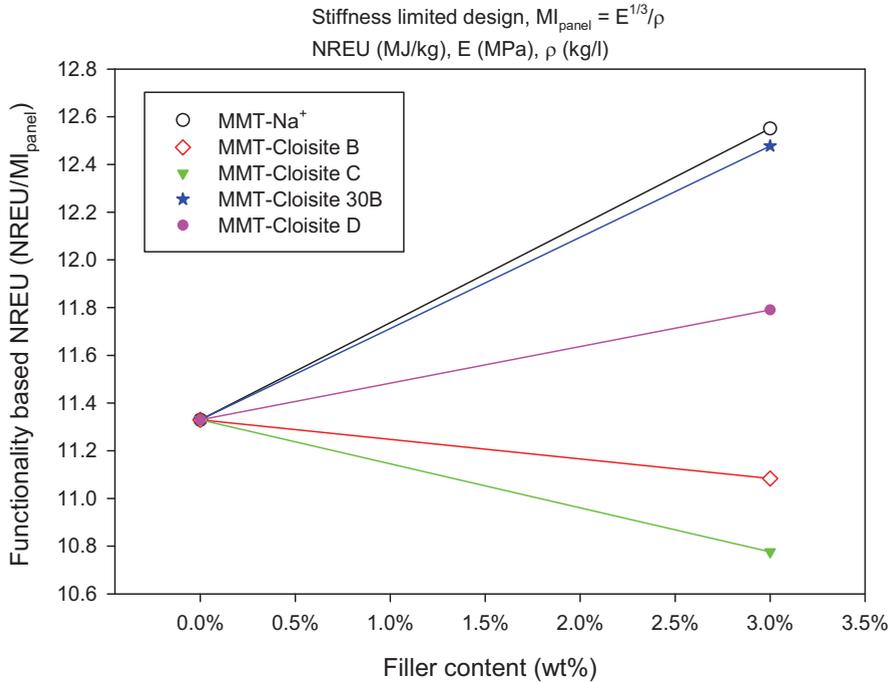


Figure 3.8: Functionality based NREU for LDPE-MMT nanocomposites if two extrusions were assumed.

3.4.3 Uncertainties

The results in this study are subject to uncertainty, mainly for two reasons: a) Data used for the calculation of the environmental impact (NREU) were estimated based on laboratory data or process data obtained from encyclopedias, engineering handbooks and LCA databases. A check with real industrial practice was not always possible; b) there is a large variety in values for Young's modulus reported by different sources.

The uncertainties regarding the environmental impact of the polymer matrices, nanoobjects, surfactants, compatibilizers and energy use could mean that the absolute values for NREU of the nanocomposites are higher or lower than presented. It could also influence the steepness of the graphs (e.g. uncertainties in NREU of nanoobjects are more pronounced at higher filler content).

The values for Young's modulus appear to be very much dependent on the study from which they are taken. Various studies report completely different values for similar

nanocomposites, but the way the nanocomposites are prepared is also different in each study. The Young's modulus and the way of producing the nanocomposite are related. Moreover, the Young's moduli reported for neat polymers sometimes also differ substantially. For these reasons, when determining the functionality based environmental impact, the Young's modulus should always be taken from the study on which the environmental assessment is based (different production methods lead to different values for the Young's modulus). The same holds for the tensile strength.

In order to quantify the uncertainties in the analyses of this study, we estimated the uncertainties of different parameters leading to the functionality based NREU. We then applied these uncertainties in the calculations, leading to upper and lower values for the functionality based NREU. Since we studied over twenty different types of nanocomposites, uncertainty analyses of all nanocomposites would be very space consuming. We therefore limited our analyses to two nanocomposites that show particularly good results. In this way we can present our most optimistic results with the uncertainty of the calculations. The nanocomposites for which we performed an uncertainty analysis are Ep-Si and PU-MMT. In Table 3.11 an overview is given of the uncertainties we assumed.

Ep-Si		PU-MMT	
Parameter	Uncertainty (%)	Parameter	Uncertainty (%)
Epoxy resin	+10 / -10	PU	+10 / -10
Jeffamine	+20 / -20	MMT	+100 / -50
TEOS	+20 / -20	Extrusion	+200 / -50
Isopropanol	+10 / -10	Electricity vacuum oven	+200 / -50
Extrusion	+200 / -50	Young's modulus	+10 / -10
Electricity vacuum oven	+200 / -50	Electricity recovery	+20 / -20
Electricity conventional oven	+50 / -50	Heat recovery	+20 / -20
Young's modulus	+10 / -10	Energy incineration	+ 50 / -50
Electricity recovery	+20 / -20		
Heat recovery	+20 / -20		
Energy incineration	+250 / -0		

Table 3.11: Uncertainties assumed for Ep-Si and PU-MMT¹⁸.

¹⁸ Although there is a large variation in Young moduli for the same material among different studies, we assume that the uncertainty for one particular study (the study on which the analysis is based) is only determined by the accuracy of the measuring equipment. Therefore the uncertainty is assumed to be only +/-10%.

Figures 3.9 and 3.10 show the results of the uncertainty assessment. Since the slope of the lines is an indication for the improvement of the functionality based NREU with increasing filler content, there is also a ‘best slope’ and a ‘worst slope’. The steepest slope (‘best slope’) is obtained if: 1) all parameters that contribute to a negative slope with increasing filler content (e.g. the amount of polymer matrix¹⁹) are multiplied with the positive uncertainty and 2) if all parameters that contribute to a positive slope with increasing filler content (e.g. the amount of filler) are multiplied with the negative uncertainty. For the flattest slope (‘worst slope’) the inverse assumptions have been applied. In Figures 3.9 and 3.10 the dashed lines represent these slopes. The solid lines represent the upper and the lower boundary of the results, if recalculated with the uncertainties assumed in Table 3.11. The colored line is the original result. In Table 3.12 the results of the uncertainty analysis are quantified. The absolute improvement is estimated from the lines determined in Figures 3.9 and 3.10.

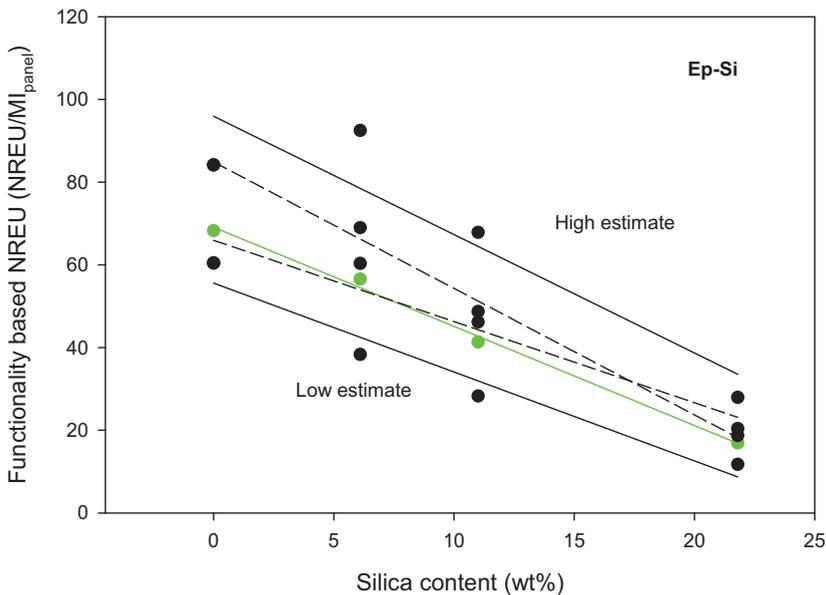


Figure 3.9: Uncertainty analysis of Ep-Si.

¹⁹ The amount of polymer matrix decreases with increasing filler content. Therefore, the contribution of the polymer matrix to the total environmental impacts and thus to the functionality based NREU decreases with increasing filler content. It therefore contributes to a negative slope of the line.

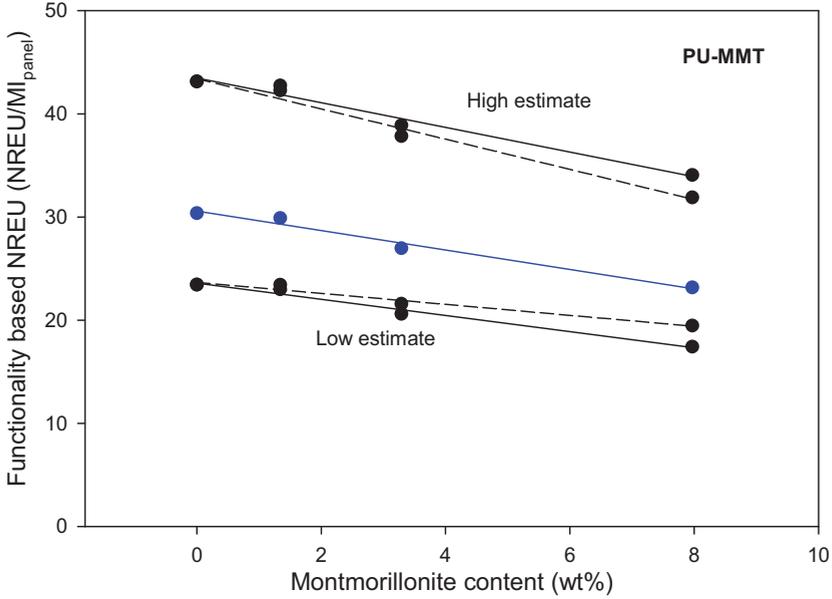


Figure 3.10: Uncertainty analysis of PU-MMT.

Nanocomposite	Absolute improvement ²⁰ (%)	Slope ²¹ (%/%)	Slope (MJ·kg·MPa ^{-1/3} ·dm ⁻³ ·% ⁻¹)	Uncertainty of the slope (MJ·kg·MPa ^{-1/3} ·dm ⁻³ ·% ⁻¹)	Uncertainty of the slope (%)
Ep-Si	65-85	-3.5	-2.4	+ 0.4 / -0.7	+ 18 / -28
PU-MMT	18-27	-3.0	-0.9	+ 0.4 / -0.5	+ 45 / -55

Table 3.12: Quantitative results of the uncertainty analyses.

²⁰ For each of the lines in Figures 3.9 and 3.10 the absolute improvement was determined by calculating the difference in functionality based NREU at the end of the lines and the beginning of the lines. This difference was expressed as the percentage improvement compared to the initial value (at 0% filler). Since for each line the absolute improvement is different, this explains the ranges for absolute improvement.

²¹ The slope is determined 1) as the percentage improvement per percentage increase of filler (%/%), 2) as the absolute improvement per percentage increase of filler (MJ·kg·MPa^{-1/3}·dm⁻³·%⁻¹).

Table 3.12 shows that the absolute improvement is highest for Ep-Si and the uncertainties are lower than of PU-MMT. The slope (relative improvement) is steepest for Ep-Si. The slope is flattest for PU-MMT and the uncertainties are highest. The absolute improvement of PU-MMT is much lower than of Ep-Si, but Ep-Si has exceptional improvement compared to all other nanocomposites. As is shown by Fig. 3.3a-d and 3.4a-c, the absolute improvement of PU-MMT is comparable to, to higher than all other nanocomposites. We estimate that the uncertainties for PU-MMT are representative also for the other nanocomposites that have not been covered by this uncertainty analysis, because their production and, hence, the involved parameters are comparable. For the nanocomposites using carbon nanotubes as filler, the uncertainties could be higher, as was revealed in Paragraph 3.2.2.3.

The present study focuses on nanocomposites that are used in stationary applications (no energy is accounted for in the use phase). If, however, they were used in mobile applications (such as car panels), then a certain fraction of the energy used in the application (such as fuel in a car) is allocated to the nanocomposite. This would change the results (being to the advantage of the material with the best mechanical properties). For examples, see [2].

It should also be noted that many more nanocomposites are currently being developed than included in this study. Our aim was to study just a representative subset of nanocomposites. For example, with respect to PHB, research involves the production of PHB co-polymers, which show better mechanical properties than PHB homopolymer (strong and not brittle) [58]. The reinforcement of these PHB co-polymers with nanoobjects is currently being studied (for example [59]). Therefore, if research continues, it is recommended that the present study is extended when new nanocomposites have been developed with improved technology.

3.5 Conclusions

In the present study, we developed and applied an indicator that addresses both the environmental impacts of nanocomposites (represented by the NREU) and its material properties. With the help of this indicator - the 'functionality based NREU' - we were able to assess the potential benefits of using nanoobjects to reinforce polymers compared to unfilled (neat) polymers or conventionally filled polymers. The main question was whether the addition of nanoobjects to a polymer matrix increases the mechanical properties to the extent that a possible increase in environmental impacts caused by the nanoobjects is compensated for or, ideally, overcompensated. To this end, we assessed the NREU of twenty-three different nanocomposites and three conventional composites.

The environmental impacts of organophilic montmorillonite, silica and carbon nanotubes (all fillers used in the nanocomposites) were determined separately.

The conclusion is that the addition of nanoobjects to polymers can have a positive effect on the functionality based NREU; we found that this was the case for PC-MMT, LLDPE-MMT, PTT-MMT, HDPE-MMT, TPS-MMT, EP-Si, PCL-MMT, PU-MMT, XLDPE-MMT, LDPE-MMT, Nylon 66-MMT, PET-MMT, Nylon 6-MMT, PLA-Si, PMMA-MWNT, NR-MMT, EPDM-SWNT and PVC-MMT. In the best cases, the improvement is 3 to 6 percent per percent increase of filler²² (the average of the nanocomposites with a negative slope is 2.4 percent improvement per percent increase of filler).

The addition of organophilic montmorillonite to natural rubber results in much lower functionality based NREU compared to unfilled natural rubber or natural rubber filled with unmodified montmorillonite or carbon black. In other cases, however, there were no benefits. For example, the use of organophilic montmorillonite in PHB nanocomposites resulted in higher functionality based NREU compared to unfilled PHB or PHB filled with sugar cane bagasse. Furthermore, the use of organophilic montmorillonite in PP-MMT and PLA-MMT, the use of CaCO₃ in PVC-CaCO₃ and the use of carbon nanotubes in PS-SWNT did not result in lower functionality based environmental impacts. It should, however, be emphasized that the uncertainties are substantial. In the case of PU-MMT, for which we assume the uncertainties to be comparable to most of the other nanocomposites, the relative improvement (slope of the line) is subject to a maximal uncertainty of + 45% / - 55%.

The data for all present analyses originate from current (often early lab-scale) technology. This means that material properties might still be inferior to what will be feasible when technology matures. Since there is still large variation in mechanical properties among different studies, further research is urgently required in order to get a better grip on the mechanical properties of nanocomposites and their determining factors.

If also the environmental impacts of the preparation of the nanocomposites can be reduced (e.g. by being more energy-efficient) the use of nanoobjects as filler might become beneficial also for nanocomposites which were found to be disadvantageous in this study.

Based on our results, we consider overall savings of 20% for NREU to be feasible for nanocomposites compared to unfilled polymers. It is recommended to further exploit this potential in parallel to investigations on health and safety which have not been studied in this paper.

²² Best cases (% improvement of functionality based NREU per % increase in filler): Ep-Si (3.4 %/%), TPS-MMT (3.5 %/%), HDPE-MMT (3.6 %/%), EPDM-SWNT (5.4 %/%) and LDPE-MMT (5.7 %/%).

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CHAPTER 4

Preliminary assessment of the risks related to the waste management of polymer nanocomposites

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Abstract

If nanotechnology proves to be successful for bulk applications, large quantities of nanocomposites are likely to end up in municipal solid waste incineration (MSWI) plants. Various studies indicate that nanoobjects might be harmful to human health and the environment. At this moment there is no evidence that all nanoobjects are safely removed from the off-gas when incinerating nanocomposites in MSWI plants. This paper presents a preliminary assessment of the fate of nanoobjects during waste incineration and the ability of MSWI plants to remove them. It appears that many primary and secondary nanoobjects arise from the incineration of nanocomposites and removal seems insufficient for objects that are smaller than 100 nm. For the nanoobjects studied in this paper, risks occur for aluminium oxide, calcium carbonate, magnesium hydroxide, POSS, silica, titanium oxide, zinc oxide, zirconia, mica, montmorillonite, talc, cobalt, gold, silver, carbon black and fullerenes. Since this conclusion is based on a desktop study without accompanying experiments, further research is required to reveal which nanoobjects will actually be emitted to the environment and to determine their toxicity to human health.

4.1 Introduction

The use of reinforcing additives in polymers is a widely known technology that has been applied for decades. Reinforcing additives are materials, which, when embedded in a polymer matrix, result in an increase in the tensile strength and the tensile modulus of elasticity of the composite compared to the neat matrix. Very common reinforcing additives in the micrometer scale have been glass fibers, carbon fibers, organic aramid fibers and natural wood fibers. [1]

A new type of materials for the reinforcement of polymers involves nanoobjects. Nanoobjects are objects that have at least one dimension in the order of 1-100 nanometer (1 nanometer = 10^{-9} m), comprising nanoparticles that are nanoscale at three external dimensions, nanofibers that are nanoscale in two external dimensions and nanoplates that are nanoscale on one external dimension. [2]

The use of nanoobjects for reinforcement of polymers has raised high expectations since it has shown to improve the mechanical properties significantly. Furthermore, it has been shown that the use of nanoobjects as reinforcing additive can have potential benefits also from an environmental point of view [3]. It is therefore expected that, when the technology has matured, it will be applied on a large scale in the near future and ‘polymer nanocomposites’ will be produced in bulk quantities.

Nanoobjects that are incorporated in polymer nanocomposites might pose a severe risk to human health, if they are released to the environment as free nanoobjects. As we will discuss in this article, there are indications that free nanoobjects change physiological mechanisms and may hence have negative impacts on human health and the environment (Section 3). Given this situation, the precautionary principle requires that measures are taken to avoid the release of free nanoobjects.

Although it may require challenging technical measures [4, 5], it is likely that the release of nanoobjects during the *production process* can be avoided to a large extent. Similarly, we expect that the release of free nanoobjects in the *use phase* is of minor importance because they can be assumed to be firmly embedded in the polymer matrix (exceptions may be products which are subject to abrasion or used under chemically harsh conditions). In contrast, the waste stage could be a potential source of free nanoobjects²³. Since it is very probable that a substantial share of the polymer nanocomposites will

²³ An additional risk might be the collection of the waste. If this occurs with compacting trucks, there is a risk of abrasion and, hence, a release of nanoobjects. This will not be treated in this study, but is recommended for further research.

ultimately be incinerated once their useful life has come to an end, it is essential that the emission of free nanoobjects is avoided²⁴.

At this moment, it is not fully clear whether waste incinerators have the ability to completely remove the nanoobjects from the off-gases, thus avoiding nanoobject emissions to the environment. The aim of this study therefore is to conduct a first prospective review of possible risks of free nanoobjects as a result of incomplete removal by municipal solid waste incineration (MSWI) plants.

In Section 4.2, the approach of this study is explained. In Section 4.3, a short review of the toxicology of nanoparticles is given. Section 4.4 deals with municipal solid waste incineration and processes that determine the fate of nanoobjects. In Section 4.5, the results of this study are outlined. Section 6 is the discussion and Section 4.7 summarizes the most important conclusions of this prospective risk assessment and directions for further research.

4.2 Approach

In order to identify possible risks of nanoobject emissions after municipal solid waste incineration, the waste incineration process is studied and discussed in this paper. Information on the processes was obtained by means of a literature survey and from the municipal solid waste incineration plant in Amsterdam, Netherlands ('Afval Energie Bedrijf - AEB'). We focus on the processes that are responsible for the fate of nanoobjects. This could be e.g. destruction or conversion in the incineration stage or possible removal during off-gas treatment. For each of these processes, the conditions that determine the fate of the nanoobjects are identified. A decision tree is constructed that provides a general methodology for the risk assessment of nanoobjects when they are incinerated in a municipal solid waste incineration plant.

As a next step, information was gathered on a subset of nanoobjects, involving data on chemical composition and size. These are important factors that determine the fate of the nanoobject during the treatment in a MSWI facility. For example, the size of the nanoobjects determines whether or not they are removed by off-gas filters, whereas the chemical composition determines whether or not the nanoobject is oxidized or undergoes other chemical reactions, or whether it remains inert. Using the decision tree it is determined which nanoobjects possibly leave the grate incineration process and to what

²⁴ When polymer nanocomposites are recycled, polymers containing nanoobjects might be mixed with virgin polymers. In such case, also the incineration of conventional polymers could entail a risk.

extent they are removed in the off-gas treatment section (with high or low efficiency). In this way, possible risks of nanoobject emissions are identified.

It should be noted that the analysis in this study is a preliminary risk assessment, which should formulate first warnings and suggestions for further research. The study was desktop-based, and no experiments have been carried out.

Before the analysis on the waste incineration process, we give a short review on the toxicity of nanoobjects in Section 4.3.

4.3 Toxicity of free nanoobjects

The main purpose of this section is to provide an overview of the possible health risks of free nanoobjects. It does not claim to be a complete literature review of the published studies on health risks of nanoobjects, but it explains the main mechanisms and indicates their impacts using concrete examples. For a more extensive review, we refer to Savolainen et al. [6].

In our daily lives, we are surrounded by nanoobjects. A normal room can contain 10,000 to 20,000 nanoobjects per cm^3 . In a forest, this can be 50,000 nanoobjects per cm^3 and in urban streets it can even be 100,000 nanoobjects per cm^3 . These levels are not necessarily harmful [7, 8]. However, exposure levels and, hence, risks might increase, when nanocomposites are produced in bulk quantities and if harmful nanoobjects are not removed during waste management.

The risks that nanoobjects represent for human health are determined by their toxicity, persistence in the environment, and bioaccumulation. In general, humans can take up nanoobjects by means of inhalation, ingestion, or, in some cases, absorption through the skin. When nanoobjects are inhaled, they can affect the human body in two major ways [7, 9, 10]:

- they can induce inflammation of the respiratory tract and cause tissue damage and subsequent systemic effects or
- they can be transported through the bloodstream to other vital organs or tissues in the body where they may cause cardiovascular and extrapulmonary complications.

Normally, uptake via the skin rarely occurs although the risk may be higher for individuals whose skin is damaged by, for example, the sun or eczema. Penetration through the skin can lead to cell damage, since nanoobjects can facilitate the production of reactive molecules. The composition, size, and surface characteristics of the

nanoobjects determine their distribution in the body. Durable, biopersistent nanoobjects may accumulate in the body, in particular in the lungs, brain, and liver.

It has been shown that the presence of nanosized ceramic and metallic particles is likely to modify the function of human macrophages [11]. This is a crucial result because macrophages represent the first line of the immune defense: they attack intruders and cause inflammation (M1 type) and they have an important role in vascular repair (M2 type). A good balance between these two functions is important in order to avoid the risk of deficiency to attack intruders on the one hand and the risk of continuous inflammation on the other. Lucarelli et al. [11] conducted *in vitro* experiments with naïve macrophages, i.e. macrophages that have not yet reached the development stage M1 or M2. They found that SiO₂ nanoobjects strongly biased naïve macrophages towards inflammation (M1 polarisation) and that also cobalt (Co) nanoobjects promote inflammatory mechanisms. Conversely, ceramic nanoobjects of titanium and zirconium were found to have an overall anti-inflammatory effect.

It has also been shown by Muller et al. [12], Jia et al. [13] and Poland et al. [14] that carbon nanotubes exhibit great respiratory toxicity. Muller et al. showed that carbon nanotubes persist in rat lungs, induce an inflammatory response and induce lung fibrosis. Jia et al. showed that carbon nanotubes damage alveolar macrophages, which are responsible for the removal of (possibly toxic) particles that are inhaled with air. Poland et al. showed that carbon nanotubes in fact show a pathogenicity that is similar to asbestos.

MohanKumar et al. [15] studied the influence of fine and ultrafine particulate matter (PM) on the brain and nervous system. They found that PM exposure induces inflammation reactions in the brain and, as a result, an increase of the stress hormone cortisol. PM can also reduce the cellular energy of cells and cause depolarization of the mitochondrial membrane, which marks the opening of the permeability transition pore. This is the beginning of apoptosis (i.e. ‘programmed cell death’). By entering cells, PM can damage DNA. It was found, that most prominent genes affected by PM were related to inflammatory processes of the brain and were associated with signalling of innate immune markers.

Nanoobjects have also been shown to exhibit ecotoxicity. For example, Lin and Xing [16] and Doshi et al. [17] showed that exogenous nanoobjects, containing zinc and aluminium, exert toxic effects on germination and growth of roots in the seedlings of six agriculturally relevant plant species. Baun et al. [18] indicated the toxicity of C₆₀, carbon

nanotubes and titanium dioxide to an aquatic invertebrate, *Daphnia magna*. Furthermore, titanium dioxide nanoobjects exert genotoxic and cytotoxic effects on fish cells [19, 20].

To summarize, the main toxic effects of nanoobjects involve damage to the immune system, respiratory toxicity, cardiovascular toxicity, cytotoxicity, damage to the brain and nervous system and ecotoxicity. This overview is not complete, however, and there are many more nanoobjects which are being considered for technical application, with potentially additional harmful effects. On the other hand, there may also be nanoobjects for which toxic effects have not been proven or for which the concentration is too low to cause damage. Nevertheless, this short review indicates that a health risk for humans and the environment does exist and for this reason, emissions should be avoided or reduced to the lowest possible level.

4.4 Analysis of the MSWI process related to the fate of nanoobjects

In the next paragraphs, we will give an outline of the MWSI processes that destroy, change or form nanoobjects and of processes that should be responsible for the safe removal of nanoobjects.

4.4.1 The waste incineration process

An outline of the waste incineration process is shown in Figure 4.1. This figure and information on the processes are based on [21, 22]. The waste delivery area is the location where the delivery trucks, trains or containers arrive in order to dump the waste into the bunker, usually after visual control and weighing. The dumping occurs through openings between the delivery area and the bunker. The bunker is usually a waterproof, concrete bed. The waste is piled and mixed in the bunker using cranes in order to achieve a balanced heating value, size, structure and composition of the material to be fed to the incinerator. Different types of incinerators can be applied for the thermal treatment of the waste, but in Europe approximately 90% of the installations use 'grate incinerators' (for a detailed description, see Section 4.4.2.1). The waste is discharged from the storage bunker and fed into the grate system. There, the waste is incinerated in a furnace. The solid residues are removed and cooled. During the incineration, a large amount of heat is produced, the majority of which is transferred to the off-gases. The off-gases are cooled down in a boiler which allows recovering part of the heat of combustion in the form of steam. The steam can be used as process heat for industrial activities or for the production of electricity. If the heat of a back-pressure turbine is recovered in the form of hot water, district heating is another option. The off-gases contain a wide range of pollutants that

need to be removed. Examples are nitrogen oxides, mercury, heavy metals, halogenated and polycyclic aromatic hydrocarbons, fine dust and many more. In the off-gas treatment section, these pollutants are to a large extent removed before the off-gases leave the chimney and are released into the atmosphere. Part will deposit on the boiler coils, however, and is removed as boiler ash. The European Commission has set regulations on air concentration of these pollutants. For dust (i.e. particulate matter smaller than $10\ \mu\text{m}$ - PM_{10}) the concentration in air should remain below $20\ \mu\text{g}/\text{m}^3$ (yearly average) [23, 24]. For ultrafine particles (UFP, i.e. particles smaller than 100 nm) no separate legislation has existed so far.

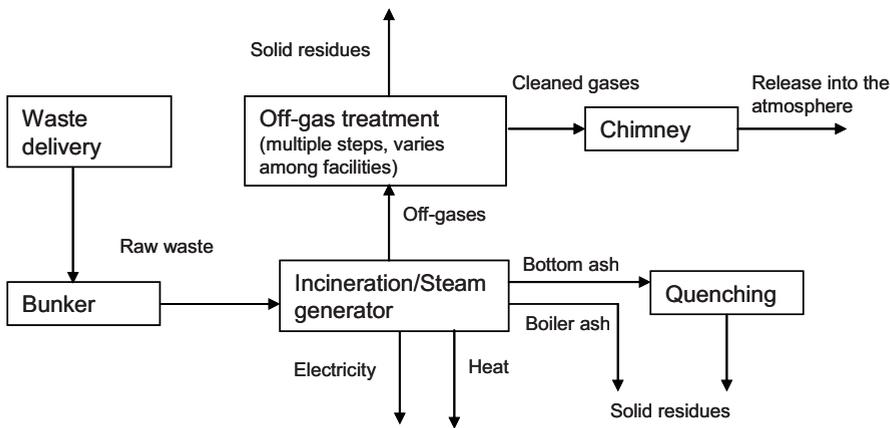


Figure 4.1: Schematic representation of the processes in a municipal solid waste incineration plant (based on [21, 22]).

4.4.2 Processes that affect the potential release of free nanoobjects

In the full process just described, there are several steps where free nanoobjects may be formed, changed or removed depending on their properties. These include the grate incineration process and several unit processes performed for off-gas treatment. These sub-processes will be described in more detail to identify the fate of nanoobjects.

4.4.2.1 Grate incineration

In grate incineration, the waste is transported along a furnace by vibrating grates. Air is fed into the system and the waste is incinerated in several stages. Figure 4.2 shows a

schematic representation of a grate furnace. Waste enters the furnace via a waste feeder. Next, the waste moves along the grate where it passes different incineration stages (see below). The waste is combusted in the combustion chamber. The solid residues (ash) are discharged in a bottom ash discharger (they are quenched in a water basin) and the off-gases leave to the off-gas treatment section.

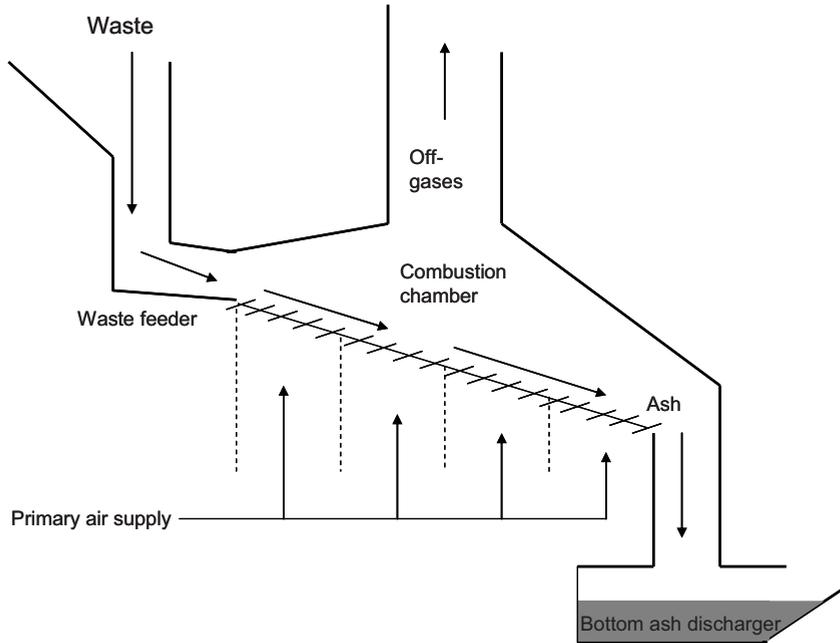


Figure 4.2: Schematic representation of a grate incinerator.

With the waste moving along the grate, the waste is incinerated in various stages. The stages in the incineration process are: drying, degassing, ignition, gasification, combustion and burn out. Details are given below (taken from [25]).

Drying: In this stage, the waste is heated to 100 °C and the water content of the waste evaporates. In order to remove the vaporized water from the waste bed, air is injected. The required energy for this process comes from the combustion zone in the form of radiation. Oxygen is not required in this stage.

Degassing: The temperature of the waste bed increases to 250 °C and the drying stage gradually phases out. As a result, evaporating carbohydrates split off and low temperature smoulder gas is generated. The energy needed for this stage, again comes from the combustion zone in the form of radiation. Because there is no combustion in this stage, there is no need for oxygen. The redox conditions have a reducing effect.

Ignition: In this stage, the released smoulder gases catch fire. Oxygen is required in this stage. During ignition, the redox conditions have a reducing effect.

Carburation/gasification: Due to the high temperatures caused by the combustion process, the solid fraction of the waste decomposes and fuel gas is generated. Carbon that was previously bound in compounds now separates and oxidizes. Although easily oxidizable materials oxidize in this stage, the redox conditions generally have a reducing effect due to the small amount of oxygen present. The temperature in the waste bed in this stage is about 400 °C.

Combustion/incineration: The smouldering gases from degassing and carburation/gasification combust with injected oxygen (primary and secondary air). The combustion temperature is around 1000-1200 °C. The redox conditions during combustion have an oxidizing effect.

Burn out: In this stage the fire dies down. Some compounds might still glow. This is the last stage of the incineration process. The redox conditions have an oxidizing effect.

The processes just described determine to a large extent whether nanoobjects are released into the off-gas treatment section. Regarding nanoobjects emerging from the incineration process, four situations are relevant:

- 1) Nanoobjects that are present in a nanocomposite are destroyed in the grate furnace.
- 2) Nanoobjects that are present in a nanocomposite are not destroyed in the grate furnace and leave with the fly ash or end up in the bottom ash.
- 3) Nanoobjects that are present in nanocomposites are destroyed (e.g. by oxidation or reaction with HCl) but they form new nanoobjects (e.g. oxides, chlorides).
- 4) As a results of incineration of (any type of) waste, new nanoobjects are formed.

We will now discuss each of these pathways.

Nanoobjects are destroyed in the furnace

If nanoobjects are combustible, i.e. if they react with oxygen, or they can be gasified, the reaction products might be gases and/or liquids that do not form any threat anymore to humans or the environment. For example, a nanoobject that consists of carbon only (such as carbon black) can be oxidized to carbon dioxide (CO₂). CO₂ (g) does not involve toxic health risk such as nanoobjects and from a toxicity point of view it can be safely emitted into the environment.

Nanoobjects are not destroyed in the furnace

Some nanoobjects might be particularly stable at high temperatures and they can leave the incineration stage unaffected. This might be true for inert nanoobjects with a very high boiling point or decomposition temperature. Other nanoobjects are not reactive, because they already consist of oxides and therefore do not further oxidize. Another possibility is when the polymer matrix in which they are embedded does not combust or decompose. In this case, the nanoobject might decompose, but it remains trapped inside the matrix and leaves the incinerator as such together with the fly ash or it ends up in the bottom ash. Finally, light nanoobjects might be transported out of the furnace before they have reacted as a result of a strong combustion air stream that is blown into the furnace.

Nanoobjects are destroyed, but they result in new nanoobjects

In many cases the nanoobjects will be destroyed. The destruction can be a result of oxidation, reduction, pyrolysis or a chemical reaction with other substances in the waste, such as acids. This will always result in new (reaction-) products which could be gaseous or liquid (as discussed above) but could also be solid and as such form a secondary type of nanoobjects. For example, CaCO₃ can be decomposed into CaO and CO₂, with CaO being a newly formed nanoobject. Nanoscale oxides can also be further reacted with acids such as HCl. For example, ZnO + 2HCl gives ZnCl₂ + H₂O. Depending on the redox conditions (reducing or oxidizing environment), elemental metals can be formed, as well as e.g. sulfides, sulphates, phosphates, fluorides and other minerals. Reactions can take place within the waste bed, in the gas phase above the bed or further downstream.

As a result of incineration, new nanoobjects are formed also from waste that is free of nanoobjects

During the incineration of waste, numerous materials are combusted and many elements are reduced/oxidized. As a result, regardless whether it concerns nanoobjects or other types of waste, new nanoobjects are formed continuously, such as metal oxides and salts or soot particles.

Given these pathways, the incineration of nanocomposites appears to be an important (even though not the only) source of free nanoobjects, especially when the amount of nanocomposites and, hence, the amount of nanoobjects in the waste increases. Although some nanoobjects might be converted into harmless substances, this will not hold for many of the nanoobjects entering or leaving the grate furnace. Whether free nanoobjects will be released into the atmosphere hence depends on the ability of the off-gas treatment section to remove them from the off-gas.

4.4.2.2 Off-gas treatment

Off-gas treatment involves many processes and techniques most of which are not relevant for particulate matter removal. However, also for particulate matter removal, several techniques exist. We will base our assessment on the techniques applied by the municipal solid waste incineration plant in Amsterdam, because this facility uses state of the art technology. The waste-to-energy-facility uses ‘electrostatic precipitators (ESP)’, ‘fabric filters’ and ‘ionization wet scrubbers’. A description of each of these technologies will be given below.

Electrostatic precipitators

An electrostatic precipitator is a particulate collection device that uses the force of an induced electrostatic charge to remove particles from a flowing gas (such as air). In principle, a precipitator contains a row of thin vertical wires, followed by a stack of large flat metal plates oriented vertically. An electric potential of several thousand volts between wire and plate is applied to ionize the gas around the electrodes, a phenomenon known as ‘corona discharge’. As a result of negative corona charge, negative ions flow to the plates and charge the gas-flow particles. The ionized particles move to the grounded plates as a result of the electric field created [26, 27]. The electrostatic precipitator safely removes most particles with a size $> 3\text{-}10\ \mu\text{m}$ (3,000-10,000 nm). [28]

Fabric filters

Fabric filters, also called baghouse filters, are widely used in waste incineration plants. Fabric filters use filtration to separate particulate matter from dusty gases. Gases containing dust enter the baghouse and pass through fabric bags that act as filters. The bags can be of woven or felted cotton-, synthetic-, or glass-fiber material. The fabric primarily provides a surface on which dust particulates collect. These particles are trapped (they stick to the fibers) through a combination of the following four mechanisms [29]:

1. *Impaction*: With this mechanism, particles having too much inertia due to size or mass cannot follow the airstream as it is diverted around a filter fiber. This mechanism is responsible for collecting larger particles.
2. *Interception*: As particles pass close to a filter fiber, they may be intercepted by the fiber. Again, this mechanism is responsible for collecting larger particles.
3. *Diffusion*: Small particles are constantly bombarded by air molecules, which cause them to deviate from the airstream and come into contact with a filter fiber, which intercepts them. This mechanism is responsible for collecting smaller particles.
4. *Electrostatic attraction*: Oppositely charged particles are attracted to a charged fiber. This collection mechanism does not favor a certain particle size.

Particle removal may be most effective down to a size of 0.1 μm (100 nm). Efficiencies for particles between 0.1 μm and 5 μm are estimated to be ~99% for one of the most efficient fabric filters, i.e. the ‘high efficiency particulate air (HEPA)’ filter. At particle sizes above 5 μm the efficiency is practically 100% [30]. However, at particle sizes below 0.1 μm the efficiencies of the filters are significantly reduced [21]. Diffusion predominates below the 0.1 μm diameter particle size. Impaction and interception predominate above 0.4 μm . In between, near the 0.3 μm , diffusion and interception predominate. For particle sizes below 0.1 μm , the effectiveness of particle removal depends on the operation mode of a MSWI. A layer of particulate matter on the fabric filter may allow removing particles down to a size of 0.01 μm (10 nm). However, this depends the operation periods between the replacement or cleaning of the fabric filter which, in turn, may be determined by parameters such as the maximum accepted pressure drop. Moreover, the removal of particles may not be safe because the layer is not sufficiently effective at all points of the filter. Furthermore, the retention of nanoobjects is not safe before the particulate matter layer has developed after replacement or cleaning of the fabric filter. [21, 29]

Ionization wet scrubbers

In a wet scrubber, the off-gas stream is brought into contact with a scrubbing liquid (usually water), e.g. by spraying it with the liquid, in order to remove the pollutants. An ionization wet scrubber system combines the mechanisms of an electrostatic filter and a scrubber. In the scrubber, a high voltage zone is installed. In this zone, particles (dust, aerosols, submicron particles) contained in the off-gas are ionized. The negatively charged particles induce opposing charges on the neutral surface of the scrubbing liquid (water) and the liquid drops. The particles then serve as a nucleus for condensation to droplets of micrometer scale. As a result, they are washed out [21]. Ionization wet

scrubbers have the ability to remove extremely small particles (<100 nm). However, only part of the particles is removed in this way, i.e. around 65% of 100 nm particles and less than 50% for particles smaller than 50 nm [31].

In conclusion, although the off-gas treatment section has the ability to remove a significant share of particulate matter, the efficiency is severely reduced for particles smaller than 100 nm. This means that part of these nanoobjects penetrates the fabric filters and ionization wet scrubbers and there is a great chance that they are emitted into the atmosphere. Zeuthen et al. [32] have estimated the total penetration of particles smaller than 100 nm after off-gas treatment to be up to 20% (based on number), depending on their size.

Solid residues

The incineration of waste results in a considerable amount of solid residues. These residues include the discharged bottom-ash from the incineration process, the removed fly-ash from the off-gas treatment section and deposited ash at the boiler coils. The bottom ash, the fly-ash and the boiler ash can contain a high amount of nanoobjects. Especially the solid residues from the off-gas treatment section contain the removed nanoobjects that have left the incineration zone with the fly ash. The solid residues are usually landfilled or used as construction material (e.g. as road base). Because of the high content of pollutants, it is very important that the solid residues are pretreated: It should at all times be avoided that the nanoobjects leach into the environment with the risk that they end up in groundwater, and hence, in drinking water. Several types of treatment exist for the solid residues. They can be solidified using binder reagents such as cement, lime, bitumen/asphalt, paraffin or polyethylene. They can also be treated thermo-chemically at high temperatures. Vitrification is a process where the residues are converted into a glassy matrix by treating them with temperatures above 1400 °C. After cooling down, a glass like or stone like product is obtained. Optionally, slow and controlled cooling allows crystallization of the melt, leading to a multi-phase product. In sintering, the residues are heated to a level (around 900 °C) where the chemical phases in the residues reconfigure, leading to a denser product with less porosity and a higher strength than the original product. To avoid leaching of heavy metals, chemical stabilization can be applied. This concept involves binding heavy metals in more insoluble forms than they are present in the original residues [21]. Since nanoobjects might be present in highly increased concentrations in the near future due to foreseen widespread use of nanocomposites, it is not guaranteed that the currently applied treatment options of solid residues prevent the leaching of nanoobjects.

4.4.2.3 Decision tree

Based on the analysis made for the possible fate of nanoparticles during all stages of the municipal solid waste incineration process, a decision tree was constructed, including all these stages. In the risk assessment of nanoobjects, the decision tree should be applied for any nanoobject that ends up in municipal solid waste in the form of a nanocomposite and for which there are possible health risks. The decision tree is shown in Figure 4.3. For a nanoobject that is incorporated in a polymer matrix it should first be determined whether or not it is released from the polymer matrix during incineration of the nanocomposite. If so, it should be identified what happens to the nanoobject under influence of decomposition, reduction, oxidation or reaction with acids such as HCl. This should also be determined for secondary nanoobjects that are formed under influence of these processes in order to arrive at an estimate of all possible nanoobjects that arise from the incineration of nanoobjects. As a next step, the fate of the nanoobjects in the fly ash has to be determined. Part will deposit on the boiler coils. For the remaining, it has to be identified whether or not these nanoobjects are removed in the off-gas treatment section. Finally, the leaching behavior of nanoobjects in the solid residues has to be determined. A 'no risk' situation occurs, if nanoobjects are destroyed in the incineration process and no new nanoobjects are formed, or if nanoobjects stay in the bottom ash or end up in the boiler ash or if they are filtered out by the off-gas treatment section and they do not leach from the solid residues. A 'risk' situation occurs, if nanoobjects are not removed by off-gas treatment or if they leach from the solid residues.

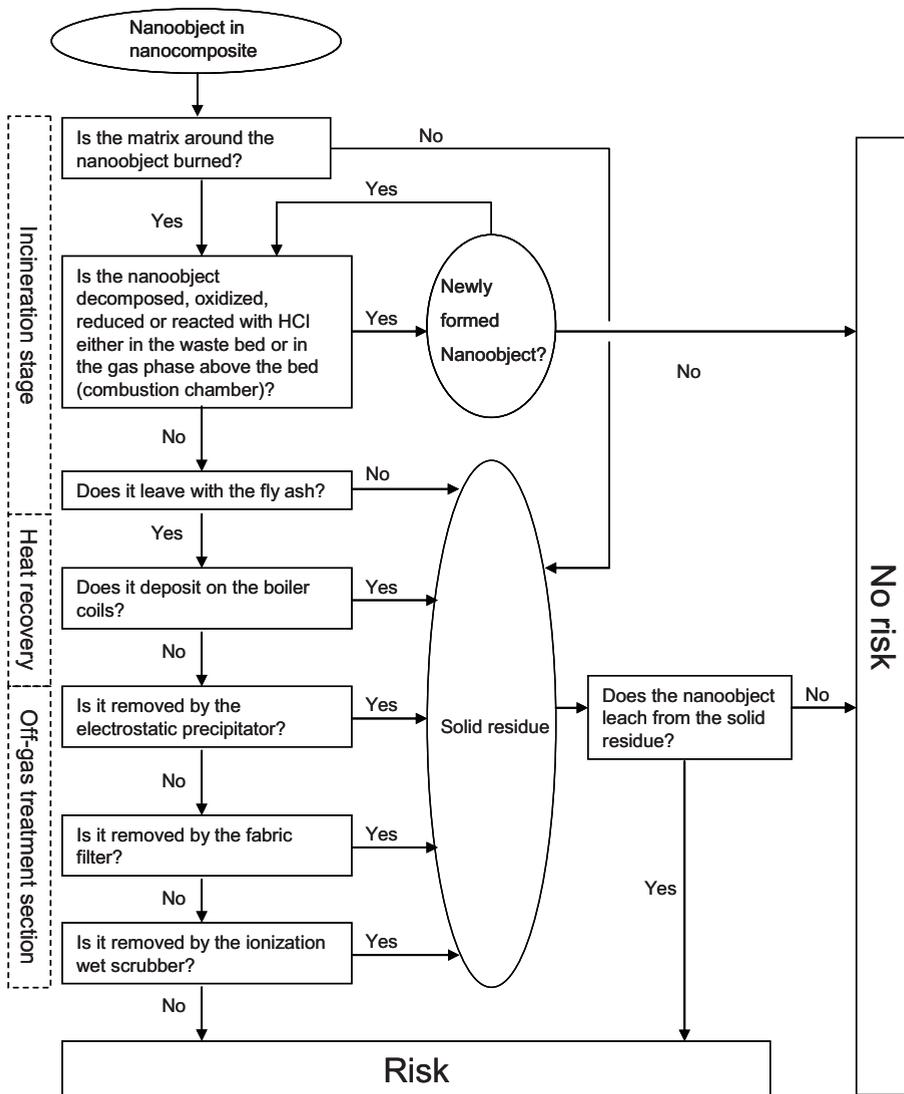


Figure 4.3: Decision tree for the determination of risks related to nanoobject releases into the environment (either from direct emission or from leaching).

4.5 Preliminary risk assessment for a subset of nanoobjects

Regarding the fate of nanoobjects in MSWI plants we summarize:

- In the grate furnace, nanoobjects can be destroyed, converted into other nanoobjects (e.g. oxides, chlorides) or leave unchanged.
- For nanoobjects that are in the range of 100 nm and larger, the efficiency of removal by electrostatic precipitators and fabric filters is highest.
- For nanoobjects that are smaller than 100 nm, the removal effectiveness is significantly reduced. These are partially removed by fabric filters and ionization wet scrubbers, but still a significant amount (up to 20%) is expected to pass (exact amount: unknown for fabric filters; more than 35-50% for ionization wet scrubbers, depending on size). Further research is needed, however, to determine the exact removal conditions of the various types of nanoobjects and the retention percentage.
- Removed nanoobjects will end up in the solid residues. Leaching from solid residues (e.g. when they are used as a construction material) should be prevented.

Nanoobject	Molecule formula	Particle size
Oxides/hydroxides		
Aluminium oxide	Al ₂ O ₃	50 nm
Calcium Carbonate	CaCO ₃	70 nm
Magnesium hydroxide	Mg(OH) ₂	15 nm
POSS	RSiO _{1.5}	Very long (size of polymer wires)
Silica	SiO ₂	10-80 nm
Titanium oxide	TiO ₂	5-40 nm
Zinc oxide	ZnO	20 -200 nm
Zirconia	ZrO ₂	20-68 nm
Minerals		
Mica ²⁵		400- 180000 nm
a) Muscovite	a) KAl ₂ (AlSi ₃ O ₁₀)(F,OH) ₂	
b) Biotite	b) K(Mg,Fe) ₃ (AlSi ₃ O ₁₀)(F,OH) ₂	
c) Lepidolite	c) KLi ₂ Al(Al,Si) ₃ O ₁₀ (F,OH) ₂	
Montmorillonite	(Na, Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ · nH ₂ O	30000 nm
Talc	Mg ₃ H ₂ (SiO ₃) ₄	1000-30000 nm
Metals		
Cobalt	Co	10-200 nm
Gold	Au	30 -150 nm
Silver	Ag	10 -500 nm
Carbon based nanoobjects		
Carbon black	C	13-95 nm
Carbon nanotubes	C	Diameter: 10-20 nm length: 500-20000 nm
Fullerenes	C ₆₀	1 nm

Table 4.1: Chemical structure and size of nanoobjects.

In Table 4.1, an overview is given of the chemical structure and particle size of a subset of seventeen different nanoobjects which are typically used as reinforcement in nanocomposites. Information of the particle size was obtained from READE Advanced Materials [33]. The fate of the nanoobjects in the incineration process depends on the redox conditions and temperature in the waste bed and in the incineration chamber. Many conversions can take place, possibly leading to secondary nanoobjects. Below, we will discuss the fate of the nanoobjects from Table 4.1 and which secondary nanoobjects we expect to arise from the incineration process. The analysis is based on the assumption that

²⁵ Many different types of mica occur. Regarding the fate of mica during incineration (i.e. decomposition behaviour), information was found for muscovite, biotite and lepidolite.

the polymer matrices around the nanoobjects are incinerated. Although the exact particle size of secondary nanoobjects is uncertain, we assume them to be nanoscale as well, i.e. smaller than 100 nm (due to the high temperatures there will be volatilization effects and only nanoscale condensation is expected). Wochele and Ludwig have calculated and evaluated the thermodynamic behavior of most elements in municipal solid waste incineration [34]. Speciation was calculated using the computer program “FLAME” [35]. Based on the thermodynamic considerations under reducing and oxidizing conditions and further literature, the behavior of the nanoobject has been assessed according to the decision tree (Figure 4.3). An extensive study on the fate of elements in incineration is given by Belevi et al. [36].

Aluminium oxide

Aluminium oxide (Al_2O_3) remains relatively stable at temperatures above 100 °C under all redox conditions. Below 200 °C AlOOH (s) is expected to form under oxidizing and reducing conditions. Under oxidizing conditions, AlPO_4 (s) is stable in the entire temperature range in the furnace (0-1200 °C) but only small quantities are expected. AlPO_4 (s) is also stable under reducing conditions, however, only below 700 °C. Under oxidizing conditions, $\text{Al}(\text{SO}_4)_3$ (s) is formed at temperatures below 500 °C. Since these are all particles with sizes below 100 nm, complete removal from the off-gas is not guaranteed. AlOOH (s) might occur primarily in the bottom ash.

Calcium carbonate

Calcium carbonate (CaCO_3) remains relatively stable at temperatures below 750-825 °C under all redox conditions. However, below 825 °C also a small amount of CaCl_2 (s) is formed. At temperatures above 600-700 °C CaO (s) is formed. CaSO_4 (s) occurs in small amounts under oxidizing conditions along the entire temperature range in the furnace (0-1200 °C). Under reducing conditions, however, a very small amount of CaS (s) is formed. [35]

Since these are all particles with sizes below 100 nm, complete removal from the off-gas is not guaranteed.

Magnesium hydroxide

At 350 °C magnesium hydroxide - $\text{Mg}(\text{OH})_2$ - is likely to decompose to MgO (s) and H_2O (g). MgO (s) occurs above 300 °C both under reducing and oxidizing conditions. Below 400 °C MgCO_3 (s) is formed. $\text{Mg}_3(\text{PO}_4)_2$ (s) is formed in low quantities over the entire temperature range (0-1200 °C) under all redox conditions. MgF_2 (s) is formed in very small amounts at temperatures below 300 °C also under all redox conditions. MgSO_4 is formed under oxidizing conditions at temperatures below 800 °C. [35]

As a result, MgF_2 (s) will occur primarily in the bottom ash where temperatures are lower. Also MgCO_3 (s), $\text{Mg}(\text{PO}_4)_2$ (s) and MgSO_4 (s) will occur in the bottom ash, but part may also leave with the fly ash. This also holds for MgO. Since it concerns particles with a size less than 100 nm, complete removal from the off-gas is not guaranteed.

Polyhedral-oligomeric-sil-sesquioxanes (POSS)

POSS molecules consist of structures representing an intermediate ($\text{RSiO}_{1.5}$) between that of silica (SiO_2) and silicone (R_2SiO). Mantz et al. [37] have studied the thermolysis behavior of POSS. At temperatures between ~ 250 - 450 °C POSS volatilizes, releasing POSS but also (volatile) decomposition products such as *c*- C_6H_{10} (g) and *c*- C_6H_{12} (g). If the volatilized POSS condenses once emitted into the environment there might be a health risk. At temperatures above 650 °C, CH_4 (g) and H_2 (g) are released. At temperatures between 600 °C – 1000 °C, SiO_2 (s) and a minor amount of SiO_xC_y (s) and SiC (s) are formed. These are secondary types of nanoobjects and might not be safely removed by the off-gas treatment system if they are smaller than 100 nm.

Silica

Silica (SiO_2) does not further react during the incineration process. [35]

Only SiO_2 (s) leaves to the off-gas treatment. It may partially remain in the bottom ash. Since the particle size is below 100 nm, complete removal from the off-gas is not guaranteed.

Titanium oxide

Most of the titanium oxide (TiO_2) does not react further during the incineration process. Only under reducing conditions and at a temperature below 100 °C other species such as TiF_3 (s) are thermodynamically stable. TiO_2 is expected to be inert during incineration. But the particle size is below 100 nm and therefore complete removal from the off-gas is not guaranteed.

Zinc oxide

Under reducing conditions and at a temperature below 800 °C ZnS (s) is formed. At temperatures above 500 °C ZnCl_2 (g) and Zn (g) (both volatile) are formed both under reducing and oxidizing conditions. Under oxidizing conditions at temperatures below 700 °C ZnSO_4 (s) is formed. ZnO (s) occurs under oxidizing conditions at temperatures above 500 °C. [38]

As a result ZnO (s), ZnS (s) and ZnSO_4 (s) possibly reach to the off-gas treatment as solid nanoobjects (although part might stay in the bottom ash). Since particle sizes below 100 nm occur, complete removal from the off-gas is not guaranteed. ZnCl_2 (g) and Zn (g) leave as volatiles and as such have a chance to be emitted into the atmosphere. Once in

the environment, they are likely to condense to solid nanoobjects. Therefore also the formation of these two species involves a risk to human health and the environment.

Zirconia

Most of the zirconia (ZrO_2) does not further react during the incineration process. At temperatures below 100 °C under reducing and oxidizing conditions ZrF_4 (s) is thermodynamically stable. But according to [34], thermodynamic considerations at low temperatures have to be interpreted with caution. Presumably, ZrO_2 can be considered as inert. A complete removal of the nanoobjects entrained to the off-gas is not guaranteed.

Mica

Various types of mica exist²⁶. Vasilyev and Lapides [39] have studied the thermal decomposition behavior of three types of mica, i.e. muscovite, biotite and lepidolite (chemical structures: see table I). They found that these micas yield the following decomposition products when heated to 1180 °C: Al_2O_3 (s), SiO_2 (s), β -eucryptite ($LiAlSiO_4$ [s]), leucite ($K[AlSi_2O_6]$ [s]), α -kalsilite ($KAlSiO_4$ [s]) and spinel ($MgAl_2O_4$ [s]). Al_2O_3 (s) and SiO_2 (s) have been discussed above. The other decomposition products are all silicates and are expected to remain stable in the incineration process, although the exact fate could not be determined. Not all decomposition products might be completely removed by the off-gas treatment section if their sizes are below 100 nm.

Montmorillonite

Montmorillonite occurs in different forms. It can contain Na-, Ca-, Al- or Mg-cations in various amounts. It will always contain Si however. A thermodynamic analysis of montmorillonite containing Na, Ca and Al in the incineration process shows that already at low temperatures montmorillonite decomposes into various species. These include SiO_2 (s), Na_2SiO_3 (s), $NaAlSiO_4$ (s), Na_2O-SiO_2 (s), $NaH_2SiO_4-7H_2O$ (s), $CaSiO_3$ (s), and $Al_2O_3-SiO_2$ (s) [35]. Although the exact particles sizes have not been determined, it is likely that these decomposition products occur at nanoscale. Complete removal from the off-gases is therefore not guaranteed. Further research is required on the secondary nanoobjects arising from incineration of montmorillonite, taking into account various compositions of montmorillonite.

Talc

Bose et al. [40] have studied the thermal decomposition behavior of talc at high temperatures. At temperatures above ~ 775 °C, talc dehydrates and yields enstatite

²⁶ Mica have the following general chemical structure: $X_2Y_{4-6}Z_8O_{20}(OH,F)_4$, in which X = K, Na, Ca; Y = Al, Mg, Fe; Z = Si, Al.

(MgSiO₃ [s]) and quartz (SiO₂ [s]). These are both secondary nanoobjects. For SiO₂ (s) the fate in an incinerator has been determined above. Although the fate of enstatite is not completely known, it is reported to be stable at temperatures up to 1550 °C. Above this temperature it melts [41]. Reaction of enstatite with HCl seems unlikely, given Gong et al. [42]. Enstatite and quartz might not be completely removed from the off-gas if their size is smaller than 100 nm.

Cobalt

Cobalt (Co) yields very different species under reducing, or under oxidizing conditions. Under reducing conditions, CoS₂ (s) is stable at temperatures below 225 °C. Between 100 °C and 400 °C, Co₃S₄ (s) is stable. CoS (s) occurs between 300 °C and 500 °C. Co(s) occurs between 400 °C and 700 °C and above 1100 °C, whereas volatile Co (g) occurs above 1000 °C. Above 625 °C Co₂P(s) and above 700 °C volatile CoCl₂ (g) is the stable form. Under oxidizing conditions, the situation is different. Below 625 °C, CoSO₄ (s) is stable. Co₃O₄ (s) occurs at temperatures between 500 and 900 °C. Volatile CoCl₂ (g) occurs above 500 °C [35]. Reducing conditions are primarily found in the waste bed, which means that concentrations of CoS₂ (s), Co₃S₄ (s), CoS (s), Co (s) and Co₂P (s) might be higher there. All particles might also leave with the fly ash and since their sizes are below 100 nm there is a risk of incomplete removal. The volatile species might condense once in the environment (at environmental temperatures) and hence involve a secondary risk. Little is known about the fate of Co in incineration. The uncertainties are substantial.

Gold

Gold (Au) appears to be inert at all temperatures within the incineration chamber and at all conditions. The presence of HCl could result in small amounts of AuCl (g), but only at temperatures above 1500 °C. Since this temperature is not reached in the combustion chamber, we conclude that only gold nanoobjects will leave to the off-gas treatment. Gold nanoobjects, however, have a size ranging from 30-150 nm. The particles smaller than 100 nm form a risk due to incomplete removal by the off-gas treatment section.

Silver

In the incineration chamber, silver is likely to be oxidized to AgO (g) at temperatures above 700 °C. AgO (g) leaves as a volatile. It might condense, once in the environment, or decompose into Ag (s) and O₂ (g). The exact fate is uncertain. At temperatures below 400 °C, in the presence of HCl, AgCl (s) is stable. Silver nanoobjects occur at sizes between 10-500 nm. AgCl is assumed to be nanoscale as well. For the objects smaller than 100 nm, complete removal by the off-gas treatment is not guaranteed.

Carbon black

Carbon black consists of amorphous carbon which is oxidized in the incineration chamber, yielding only CO₂ (g). However, there is a great chance of incomplete combustion. Therefore, unreacted carbon black might leave with the fly ash. Since the size is smaller than 100 nm, complete removal by the off-gas treatment is not guaranteed.

Carbon nanotubes

Carbon nanotubes consist of carbon only, that yields CO₂ (g) when oxidized. However, not all carbon nanotubes might oxidize and as a result, unreacted carbon nanotubes might persist in the bottom ash or leave to the off-gas treatment section. Due to their (large) size, it is expected that they are removed from the off-gas and hence, do not end up in the environment. Leaking from solid residues should be prevented, however.

Fullerenes

Just as carbon nanotubes, fullerenes consist of carbon only and yield only CO₂ (g) when oxidized. However, unreacted fullerenes have a size around 1 nm and hence would not be completely removed by the off-gas treatment. Therefore, fullerenes in waste might form a threat.

Table 4.2 summarizes the findings from this preliminary risk assessment. It appears that the incineration of nanoobjects consisting of aluminium oxide, calcium carbonate, magnesium hydroxide, POSS, silica, titanium oxide, zinc oxide, zirconia, mica, montmorillonite, talc, cobalt, gold, silver, carbon black and fullerenes entails a risk. In contrast, the incineration of carbon nanotubes seems safe, provided that they do not leach from solid residues into the environment. It should be mentioned that all nanoobjects are assumed to partly end up in the solid residues.

	Primary nanoobject to fly ash?	Secondary nanoobject(s) to fly ash?	Complete removal by off-gas treatment?	Risk of nanoobject emission via stack?
Aluminium oxide	Yes	Yes	No	Yes
Calcium Carbonate	Yes	Yes	No	Yes
Magnesium hydroxide	No	Yes	No	Yes
POSS	Yes	Yes	No	Yes
Silica	Yes	No	No	Yes
Titanium oxide	Yes	No	No	Yes
Zinc oxide	Yes	Yes	No	Yes
Zirconia	Yes	No	No	Yes
Mica	Yes	Yes	No	Yes
Montmorillonite	Yes	Yes	No	Yes
Talc	Yes	Yes	No	Yes
Cobalt	Yes	Yes	No	Yes
Gold	Yes	No	No	Yes
Silver	Yes	Yes	No	Yes
Carbon black	Yes	No	No	Yes
Carbon nanotubes	Yes	No	Yes	No
Fullerenes	Yes	No	No	Yes

Table 4.2: Table summarizing the results of the preliminary risk assessment.

4.6 Discussion

The analysis in this study is a first preliminary assessment of risks of free nanoobjects due to incomplete removal by MSWI plants. The approach taken is based on generic assumptions that may not always reflect the complexity of the waste incineration process and the off-gas treatment. Nevertheless, the approach applied in this paper provides a first indication of risks and indicates the need for further experimental investigation and research: The highest risk for human health occurs if toxic nanoobjects are released to the environment. Further research therefore has to focus on nanoobjects that especially might form a threat. This could be done in two directions both of which should be pursued: 1) first determine for which particles there is a risk of emission by MSWI plants due to incomplete removal and next determine their toxicity to identify those particles that form a real threat, or 2) First determine which particles could be a serious threat to human health (toxicity tests) and then investigate whether there is a risk that they are released after waste incineration. Also here, reality might be more complex. For example, even non-toxic nanoobjects may turn out to be problematic. In an incinerator, volatile heavy

metal compounds will condense on the particles with a large surface area. In this way, e.g. non-reactive SiO₂ nanoparticles can become the carriers of virtually all metals present in the off-gas, which dramatically increases the risks to human health and the environment if they are emitted. See, for example, Zeuthen et al. [32].

To determine the possible release of nanoobjects by MSWI plants, we propose laboratory experiments in which the incineration and removal of nanoobjects is tested for the various methods (grate incineration, fabric filters, electrostatic precipitation, ionization wet scrubbers). For the determination of the toxicity of nanoobjects, more *in vivo* tests should be performed to identify those particles that form a serious threat to human health.

Depending on legislation and the waste management infrastructure in place, landfilling is still an option in some countries. If nanocomposites are disposed of in landfills without lining, free nanoobjects can certainly be released to the environment, while further investigations are recommended for landfills that do have a lining.

For nanocomposites with a *biodegradable* polymer matrix, digestion and composting may be considered as suitable waste management options. Both processes yield compost which is very likely to contain nanoobjects. Since the compost is meant to be used for soil amelioration, these nanoobjects would be released and there may even be a risk that they end up in the food chain. If the solid output of the digestion plant is incinerated instead of being used as compost, this would also entail a high risk of release of free nanoobjects (see discussion above on incineration). In contrast, the risks related to the combustion of the *biogas* originating from the digestion plant might be small, because it seems unlikely that nanoobjects enter the biogas phase. However, the nanoparticles would end up in the digester solids which are often used as soil conditioner or may otherwise be burnt; there is a high risk that these pathways would again lead to free nanoobjects.

4.7 Conclusions

Nanoobjects might form a serious threat to human health and the environment depending on the exposure levels and their chemical composition. With increasing production of products that contain nanoobjects, the risk for human beings to get exposed to high levels of nanoobjects increases. In our view, the future release of nanoobjects from the combustion of nanocomposites in MSWI plants is an important concern. As this preliminary risk assessment has shown, the combustion of nanocomposites results in a release of the nanoobjects (provided that the polymer matrix is burned) and often, many secondary nanoobjects may be formed as a result of reduction, oxidation, decomposition or a reaction with HCl. There seems to be a relatively high risk that current filter techniques are insufficient to remove nanoobjects with a size smaller than 100 nm. Based

on the results presented in this study, we conclude that carbon nanotubes should entail low risks. The other nanoobjects, i.e. aluminium oxide, calcium carbonate, magnesium hydroxide, POSS, silica, titanium oxide, zinc oxide, zirconia, mica, montmorillonite, talc, cobalt, gold, silver, carbon black and fullerenes result in primary and secondary nanoobject emissions. Especially the incineration of zinc oxide, magnesium hydroxide, calcium carbonate, aluminium oxide, cobalt, montmorillonite and mica yields many secondary nanoobjects. Silica and gold are not expected to form secondary nanoobjects when incinerated. Further toxicity tests should determine which particles form a particular threat. For these, safe technologies for removal should be developed. Another risk of humans getting exposed to nanoobjects, is when they end up in the food chain. This could happen if nanoobjects are released into the environment after leaching from solid residues that are landfilled or used in construction, or for nanomaterials with a biodegradable matrix, when they are digested or composted. Alternatively, nanoobjects could be deposited after release through the stack and then be absorbed by organisms. Further research is required.

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CHAPTER 5

Ex-ante environmental and economic evaluation of polymer photovoltaics

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Abstract

The use of polymer materials for photovoltaic (PV) applications is expected to have several advantages over current crystalline silicon technology. In this paper, we perform an environmental and economic assessment of polymer-based thin film modules with a glass substrate and modules with a flexible substrate and we compare our results with literature data for multicrystalline (mc-) silicon photovoltaics and other types of PV. The functional unit of this study is '25 years of electricity production by PV systems with a power of 1 watt-peak (W_p)'. Because the lifetime of polymer photovoltaics is at present much lower than of mc-silicon photovoltaics, we first compared the PV cells per watt-peak and next determined the minimum required lifetime of polymer PV to arrive at the same environmental impacts as mc-silicon PV.

We found that per watt-peak of output power, the environmental impacts compared to mc-silicon are 20-60% lower for polymer PV systems with glass substrate and 80-95% lower for polymer PV with PET as substrate (flexible modules). Also in comparison with thin film CuInSe and thin film silicon, the impacts of polymer modules, per watt-peak, appeared to be lower.

The costs per watt-peak of polymer PV modules with glass substrate are approximately 20% higher compared to mc-silicon photovoltaics. However, taking into account uncertainties, this might be an overestimation. For flexible modules, no cost data were available. If the efficiency and lifetime of polymer PV modules increases, both glass-based and flexible polymer PV could become an environmentally friendly and cheap alternative to mc-silicon PV.

5.1 Introduction

At present, most of the world production of photovoltaic (PV) cells is based on crystalline silicon. New generations of PV cells have been developed, though, based on inorganic materials like CdTe and CuInSe (CIS) [1] or mesoporous nanocrystalline TiO₂ films (dye-sensitised cells) [2]. A particularly interesting new generation of PV systems utilizes semiconducting conjugated polymers, which are also referred to as “polymer solar cells”. The principles of these polymer solar cells have been described in various articles [3-5]. They are expected to offer several advantages over silicon-based solar cells: The polymers are mechanically flexible, semitransparent and soluble in common organic solvents, where the latter characteristic allows deposition by simple solution processing and printing technologies. Developers of polymer solar cells claim it is conceivable that polymer PV systems become economically competitive in the future and that they may be more environmentally friendly to produce [6]. So far, no detailed environmental and economic assessments have been carried out for polymer PV modules, in contrast to silicon based, inorganic thin film and dye-sensitised modules [7-16]. In this paper, we study the environmental impacts and the costs throughout the life cycle of polymer-based PV systems, and compare them with crystalline silicon PV systems. Also, we performed a limited comparison with other thin film technologies. For the environmental assessment, we studied two types of polymer based PV, i.e. modules using a glass substrate and flexible modules on a polyethylene terephthalate (PET) substrate. Polymer PV modules can be produced on glass or on a flexible substrate, and, as a result, different types of polymer PV could be produced, also with different applications. It is expected that fully flexible modules eventually will find their use in charging small devices. The advantage of their flexibility could be used for easy integration in clothing or electronic devices. However for large-scale grid-connected applications, polymer cells on glass substrates may be preferred. Since, at the moment, the production of polymer solar cells is still in the laboratory stage and has not yet been commercialized, the analyses presented in this paper are prospective in nature and they are preliminary, thereby reflecting the current insight. We use information on best available technology. In this article, we use the term ‘solar cells’ for the material layers where light is converted to electricity and current is collected, whereas ‘PV module’ refers to the laminated structure of substrate, solar cell materials and cover materials. The ‘PV system’, finally, refers to (a number of) PV modules installed at the ground or on a roof-top together with connection cables, inverter and support structure.

In Chapter 5.2 we will present the environmental analysis based on the life cycle assessment (LCA) methodology. In Chapter 5.3 we present the economic analysis. Chapter 5.4 is the discussion chapter, concerning an uncertainty analysis, a sensitivity

analysis of the efficiency and a forecast on future polymer- and mc-silicon PV costs. Chapter 5.5 contains the conclusions of this study.

5.2 Environmental assessment

5.2.1 LCA fundamentals

Life cycle assessment is the most widely applied and accepted method for the environmental analysis of products and services. It is a standardized method for the compilation and evaluation of the inputs, outputs and the potential environmental impacts of a product system throughout its life cycle. The LCA methodology has been standardized by the International Standards Organisation (ISO) in the ISO-14040 series [17]. We will follow these standards (goal definition and scoping, inventory analysis, impact assessment, interpretation) in this study.

5.2.2 Goal definition and scoping

The primary goal of this LCA is to compare organic polymer-based PV systems with conventional, silicon based, PV systems on environmental impacts throughout the life cycle. The main comparison is with multicrystalline (mc-) silicon PV, since this technology has the largest market share at the moment. A comparison with thin film PV systems is made as well. For thin film, four major technologies presently exist: amorphous silicon (a-Si), cadmium telluride (CdTe), copper indium selenide or sulphide (CIS) and finally dye-sensitized cells (DSC). We calculated the impacts of polymer PV ourselves, while the impacts of silicon PV, CdTe PV, CIS PV and dye-sensitised PV are obtained from published environmental assessments. We limit our study to the production and use phase of the PV systems and exclude the waste phase. The reason for this is that there are no advanced waste treatment processes for any PV types yet; only some lab-scale and one pilot-scale operation exist. Because all considered PV module types were assumed to produce the same amount of electricity, the use phase does not influence the final results and can be disregarded in the comparison. For crystalline silicon and thin film modules we consider present-day production technologies, whereas for the polymer modules we assume best available technology as is currently used in the laboratory. As functional unit we choose:

“25 years of electricity production by PV systems with a power of 1 watt-peak (W_p)”

Assuming a 75% Performance Ratio for the PV systems and average irradiation intensities, a 1 W_p PV system will produce 0.750 kWh/yr in Central Europe (1000 kWh $m^{-2} yr^{-1}$ of irradiation) and 1.275 kWh/yr in Southern Europe (1700 kWh $m^{-2} yr^{-1}$ of irradiation).

The characteristics of the systems that are compared in this LCA are summarized in Table 5.1. The efficiencies reported are estimates based on the types used in the sources listed (there might be some variation among various types). The efficiency of the mc-silicon PV system is typical for present day mc-silicon PV modules. For all PV systems listed, the efficiencies refer to the efficiencies of the modules (the efficiencies of the individual cells might be higher, but due to space between the cells there is some efficiency loss).

	Efficiency (%)	Surface area (cm ² /W _p)	Reference
Polymer PV system	5.0	200	[18-22]
Multicrystalline- silicon PV system	13.2	76	[9]
Thin film CdTe PV system	9.0	111	[15]
Thin film CIS PV system	11.0	91	[15]
Thin film silicon PV system	6.3	159	[16]
Dye-sensitised PV system	8.0	125	[14]

Table 5.1: Characteristics of the PV systems included in this paper.

Conventional multi-crystalline silicon modules can easily achieve lifetimes of 25 years or more. For polymer solar cells, however, the lifetime thus far has been much shorter (only weeks to a few months according to [23], a little more than one year according to [24]). It is, however, expected, that outstandingly high stabilities of the conducting polymers are within reach, which will increase the lifetime of the solar cells drastically [25]. In this study, we will first determine the environmental impacts of 1 watt-peak polymer PV (glass-based and PET based) and 1 watt-peak silicon PV. Next, we will estimate the minimal lifetime that is required for polymer solar cells in order to have lower environmental impacts compared to the silicon-based solar cells. The environmental impacts we will take into account are *Non-Renewable Energy Use (NREU)*, *climate change in the next 100 years (Global Warming Potential, GWP₁₀₀)*, *abiotic depletion*, *ozone layer depletion*, *photochemical oxidant formation*, *acidification* and *eutrophication*. The calculation of environmental impacts (except NREU) follows the latest CML method [26]. In this study we do not present impacts with respect to *human toxicity*, *terrestrial ecotoxicity*, *marine aquatic ecotoxicity* and *fresh water aquatic ecotoxicity*, because the existing impact assessment methods (e.g. EDIP97, CML2001 and Eco-indicator 99) do not yield comparable results [27] and because toxicity data have been determined only for a limited number of substances, which makes the methods incomplete. Currently, the European Platform on Life Cycle Assessment and the LCA

initiative of UNEP & SETAC are working on improvement of the methodology to assess toxicity.

For the comparison of polymer PV systems with other thin film PV systems, the only impact categories taken into account are NREU and climate change, due to limited scope of the cited studies for the other thin film technologies.

5.2.3 Inventory analysis

5.2.3.1 General

A polymer solar cell consists of a substrate (glass or polymer foil) onto which several electronic layers are deposited. Photoactive polymer layers convert light to electricity and with the help of supporting materials the electric charge is transported to two metal layers, serving as the electrodes. A back foil layer protects the solar cell.

For the production of polymer solar cells, several techniques exist; there are different techniques for deposition of the photoactive layers and there is some variety in polymers to be used in these layers. Furthermore the production method for flexible modules and modules based on glass differs (flexible modules can be produced continuously with a roll-to-roll system).

In general, two deposition techniques are used: evaporation of the material and wet processing (using a solution of the material). The choice of the materials to be processed determines which technique is most suitable: for evaporation, thermal stability is required, whereas materials for wet processing need to be soluble. As a consequence, for small molecules, evaporation is the best choice, while semiconducting polymers are mainly processed from solution [5]. Since we study polymer solar cells, we will focus on wet processing.

Several wet processing deposition techniques exist (spin coating, doctor blading, screen printing and inkjet printing), but they are not equally applicable in all situations. Spin coating, e.g., is uneconomical for large areas because of the high investment costs. Doctor blading (or: gravure printing) is difficult to apply for films with a thickness of a few 100 nm; it is suitable for films of 1 μm . Screen printing is only applied to small area polymer solar cells. Inkjet printing has large potential for devices where fine circuit structures are required. It has been used successfully for organic thin-film transistors [28].

For the charge transport in polymer solar cells (the photoactive layers) several materials can be used. An overview of the most common ones is given in Table 5.2.

Hole-conducting donor polymers	P3HT poly(3-hexylthiophene-2,5-diyl)
	MDMO-PPV poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene
	PFB poly(9,9'-dioctylfluorene-co-bis- <i>N,N'</i> -(4-butylphenyl)-bis- <i>N,N'</i> -phenyl-1,4-phenylenediamine)
Electron-conducting acceptor organic materials	PCBM [6,6]-Phenyl C ₆₁ -butyric acid methyl ester
	CN-MEH-PPV (poly-[2-methoxy-5-(2'-ethylhexyloxy)-1,4-(1-cyanovinylene)-phenylene])
	F8TB (poly(9,9'-dioctylfluorene-co-benzothiadiazole))

Table 5.2: Overview of commonly used photoactive materials [5].

At present, P3HT is the most commonly used conductive polymer [18-20, 29], and together with PCBM it is currently the best performing material system for application in polymer solar cells [30-32]. Therefore, we study solar cells based on these two materials.

We will now present the inventory data of two types of polymer PV, i.e. a PV system that uses a glass substrate and a flexible module that uses PET as a substrate.

5.2.3.2 Polymer PV on a glass substrate

Shah and Wallace [33] describe the production of polymer PV cells on glass. Their description of the manufacturing process, together with information on module assembly from De Wild - Scholten and Alsema [9], and 'balance of system (BOS)' from De Wild-Scholten et al. [12] serves as the basis for the process chain in Figure 5.1.

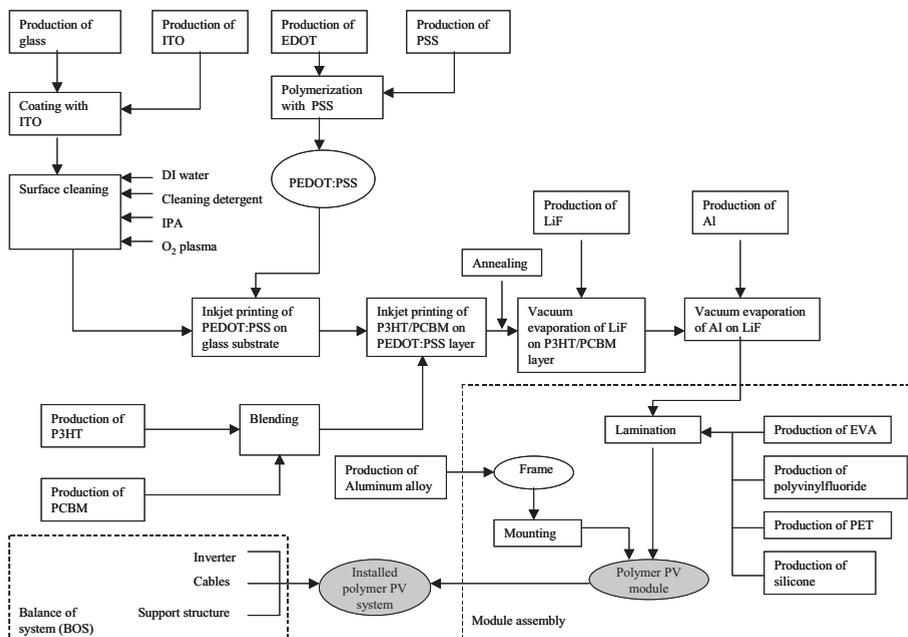


Figure 5.1: Process chain for the production of a polymer PV system on a glass substrate. (EDOT: 3,4-ethylene dioxythiophene. Other abbreviations: See text)

As first step, glass is coated with indium tin oxide (ITO). The ITO layer forms the front electrode. Then it is cleaned in an ultrasonic bath using a cleaning detergent after which it is further treated with deionized (DI) water, isopropyl alcohol (IPA) and O₂ plasma. Poly(3,4-ethylene dioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) is inkjet printed on the ITO coated substrate. This facilitates hole conduction and also smoothens the relatively rough ITO layer, which prevents short circuits in the solar cell. Next, a blend of poly(3-hexylthiophene) (P3HT) and [6,6]-Phenyl C₆₁-butyric acid methyl ester (PCBM) is inkjet printed on the PEDOT:PSS layer. P3HT serves as an electron donor and PCBM as an electron acceptor. The device is heated on a hot plate (150 °C) for 3 minutes under argon atmosphere (annealing) to increase the morphological and optical properties of the photoactive blends [34]. A layer of lithium fluoride (LiF) is evaporated onto the photoactive P3HT/PCBM layer to reduce the interface barrier for electron injection. Aluminium is evaporated onto LiF. The aluminium layer forms the back electrode of the solar cell. [33]

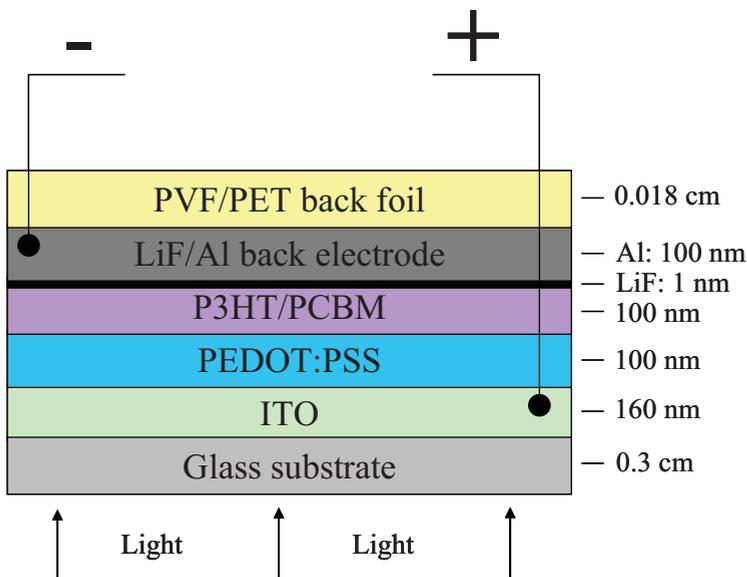


Figure 5.2: Schematic cross section of a polymer solar cell on a glass substrate.

To produce a PV *module*, the solar cells on their substrate are laminated with a combined polyvinylfluoride (PVF) and polyethylene terephthalate (PET) back cover foil²⁷. To bond the layers, ethylvinylacetate (EVA) is used. A small amount of silicone is used for the diaphragm of the laminator that has to be replaced on a regular basis. Finally, the laminate is usually mounted into an aluminum alloy frame. A cross-section of the module (excluding the frame) is shown in Figure 5.2.

To install the PV module, electricity cables are attached, as is an inverter to convert direct current into alternating current. Finally a support structure is needed to fix the system, e.g. on a roof. Cables, inverter and support structure together form the balance of system (BOS).

Tables 5.3a-d give an overview of the various material and energy requirements needed to produce a polymer PV system on a glass substrate. It is assumed that, after deposition of the photoactive layers, only 90% of the solar cell area is functioning properly. We therefore assume 10% material losses.

²⁷ the term ‘solar cells’ is somewhat misleading, since the photoactive area does not consist of multiple cells, but is in fact a monolithic area.

Material	Thickness layer ^a (cm)	Density (g/cm ³)	Weight (g)
Glass	0.3	2.58	172
ITO	0.000016	7.2	0.0256
PEDOT:PSS	0.00001	1 ^b	0.002
P3HT/PCBM	0.00001	1 ^b	0.002
LiF	0.0000001	2.64	0.00006
Al	0.00001	2.7	0.006

Table 5.3a: Materials needed for the production of a polymer solar cell on a glass substrate with 1 W_p power (all values refer to a surface of 200 cm², thereby assuming 10% material losses during manufacturing).

^a Source: [33]

^b Own estimate, similar to estimate in Hillman et al. [35]

Inputs for cleaning	Amount	Unit
Deionized water	3.06	kg
Isopropanol	0.00175	kg
Oxygen	0.00116	kg
Detergent (soap)	0.0011	kg
Electricity - plasma cleaning	0.0813	MJ
Electricity- ultrasonic bath	0.0111	MJ
Inputs for annealing	Amount	Unit
Electricity	0.053	MJ
Argon	0.001	Kg

Table 5.3b: Material and energy requirements for substrate cleaning (per W_p) [9, 36, 37] and annealing (own estimate based on [34]²⁸).

²⁸ Annealing is performed on a hot plate at 150 °C for 3 minutes under argon atmosphere. Electricity use is estimated at 40 kW/m². Argon use is estimated to be 0.89 kg.h⁻¹m⁻², thereby assuming that annealing is performed in an argon environment with a height of 50 cm and that all argon is replaced during one hour, due to losses.

Inputs for lamination	Amount	Unit
Ethylvinylacetate	0.020	Kg
Polyvinylfluoride	0.00256	Kg
PET film	0.00256	Kg
Silicone product	0.0000464	Kg
Electricity	0.48	MJ
Inputs for framing	Amount	Unit
Aluminum alloy (AlMg ₃) ²⁹	0.061	Kg

Table 5.3c: Material and energy requirements for the lamination and framing of a polymer PV module (per W_p) [9].

Inputs for balance of system (BOS)	Amount	Unit
<i>Inverter</i>		
Inverter	0.00556 ³⁰	Part
<i>Cabling</i>		
DC solar cable	0.0432	M
AC cable	0.0022	M
<i>Support structure, in-roof</i>		
Aluminium alloy (AlMg ₃)	0.0242	Kg
Chromium steel 18/8	0.0056	Kg
Polyethylene	0.000482	Kg
EPDM roofing sheeting	0.0200	m ²
Avoided product	Amount	Unit
<i>Support structure, in-roof</i>		
Roof tile	0.80	Kg

Table 5.3d: Material requirements for balance of system (BOS) of an in-roof polymer PV system (per W_p) [12].

²⁹ For this type of alloy, 80% recycled aluminum and 20% primary aluminum is used according to the ecoinvent database. We have followed this assumption.

³⁰ The power of the inverter is 300W. The lifetime of the inverter is set to 15 years [13]. Therefore 1.67 inverters are needed for 25 years of electricity production.

5.2.3.3 Flexible polymer PV on a PET substrate

The flexible polymer PV on a PET substrate differs somewhat from the module on glass. Not only is the substrate different, but usually it does not require a frame and module support either, because it will be integrated with some other product or rigid surface³¹. Information on the production process for flexible polymer modules was obtained from a manufacturer, who, for confidentiality reasons, wishes not to be referenced. An overview of the production process is shown in Figure 5.3. A cross section of the module is shown in Figure 5.4.

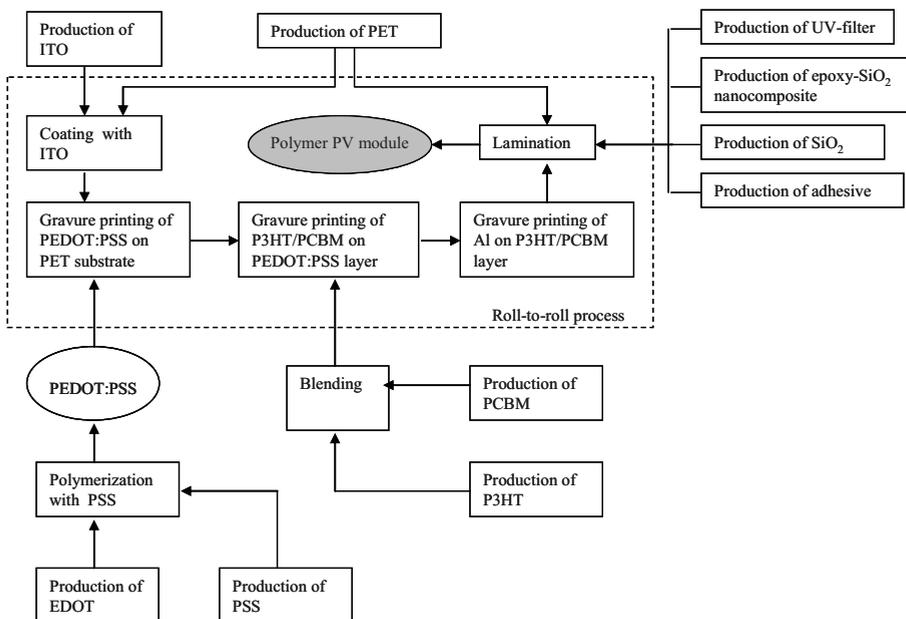


Figure 5.3: Process chain for the production of a flexible polymer PV module on a PET substrate.

³¹ We assume that the flexible polymer cells will not be placed on a roof or in a field and used for grid-connected operation, at least not in the immediate future.

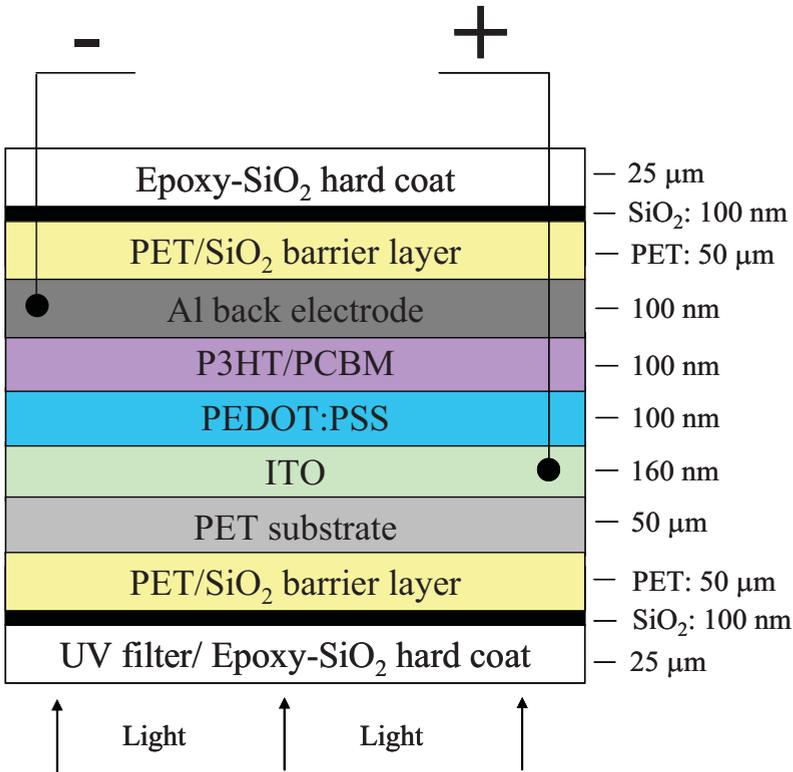


Figure 5.4: Schematic cross section of a flexible polymer solar cell on a PET substrate.

The basic materials used for the flexible module are similar as for the module on a glass substrate; ITO is used for the positive electrode, PEDOT:PSS is used for hole conduction and P3HT and PCBM are the electron donor and the electron acceptor respectively. Aluminium is used as the negative electrode, while lithium fluoride is not used in this cell. A big difference to the glass-based module, is that the flexible module is produced by a continuous roll-to-roll process. The production rate is much higher than in the batch process used for glass-based polymer module production. The PEDOT:PSS, P3HT/PCBM and aluminium layers are deposited by means of gravure printing³². The solar cells are encapsulated into two barrier layers and two hard coats. The barrier layer is

³² Gravure printing is difficult to apply for films with a thickness of a few 100 nm. However, a solvent is used, which makes the initial (wet) layers much thicker (~20 micron). The solvent is evaporated afterwards.

made of PET coated (by sputtering) with silica (SiO₂). The hard coat is made of an Epoxy-silica nanocomposite. At the front side an UV-filter (a 2-(2'-Hydroxyphenyl)benzotriazole derivative) is integrated into the hard coat.

Tables 5.4a-c display the material and energy requirements for producing a flexible polymer PV system on a PET substrate.

Material	Thickness layer (cm)	Density (g/cm ³)	Weight (g)
PET	0.005	1.33	1.48
ITO	0.000016	7.2	0.0256
PEDOT:PSS	0.00001	1	0.002
P3HT/PCBM	0.00001	1	0.002
Al	0.00001	2.7	0.006

Table 5.4a: Materials needed for the production of a flexible polymer solar cell on a PET substrate with 1 W_p power (all values refer to a surface of 200 cm², thereby assuming 10% material losses during manufacturing. Data are based on personal communication).

Energy carrier	Amount	Unit
Light fuel oil	21.5	kJ
Electricity	0.00258	kWh
Emissions to air	Amount	Unit
Toluene	0.447	G

Table 5.4b: Energy carriers needed for gravure printing (for three layers of 200 cm², assuming 10% material losses).

Materials	Amount	Unit
PET	2.66	G
SiO ₂	0.0088	G
Epoxy silica nanocomposite	0.99	G
Epoxy resin	0.185	G
UV-filter	0.002	G
Energy carriers	Amount	Unit
Electricity	0.00026	kWh
Natural gas	0.788	kJ

Table 5.4c: Materials and energy carriers for the lamination of a flexible polymer PV module (200 cm², no material losses).

5.2.3.4 Derivation of other inventory data

From material and energy requirements in each process step, environmental impacts can be calculated. For this purpose, process data for the production of these materials are needed, based on which we can derive emissions to the environment and extraction of raw materials from the environment. Many of the ‘inventory data’ required for this analysis are not readily available from life cycle assessment databases such as the Ecoinvent database (www.ecoinvent.ch). For example, for the production of the materials for the photoactive layers (PEDOT:PSS, P3HT/PCBM) and LiF, inventory data had to be estimated from publicly available literature and contact with manufacturers.

Production of PEDOT:PSS

PEDOT:PSS is produced by H.C. Starck (Leverkusen-Germany) under the name Baytron P (weight ratio PEDOT:PSS is 1:2.5). PEDOT:PSS is produced in three main steps: 1) production of EDOT (monomer) 2) production of PSS and 3) polymerisation of EDOT with PSS to PEDOT:PSS. In Figure 5.5, the chemical processes to produce EDOT are shown. From H.C. Starck [38] we obtained information on reaction temperatures, reaction times, yields, agitation, solvents and starting materials. This allowed us to derive inventory data for the production of PEDOT:PSS. We used the following assumptions³³:

- We assumed a cylindrical vessel of 160 liter with equal height and diameter.
- We estimated the heat requirements on the basis of the specific heat of the solvents (Dimethylformamide: $150.7 \text{ Jmol}^{-1}\text{K}^{-1}$, Dimethylacetamide: $175 \text{ Jmol}^{-1}\text{K}^{-1}$) and of the reaction intermediates (estimated at $115 \text{ Jmol}^{-1}\text{K}^{-1}$) and accounted for heat losses through a polyurethane insulation layer around the vessel (10 cm thickness, conductivity: $0.014 \text{ Wm}^{-1}\text{K}^{-1}$)
- We assumed electricity use for agitation to be 0.5 kW/m^3 [39].
- Energy use (steam) for distillation is estimated by multiplying the heat of evaporation of the distilled product by a reflux factor of 1.3. Electricity use is estimated at $0.1 \text{ MJ}_e/\text{kg}$ product [39].

³³ Although we have been able to derive inventory data with the assumptions made, the calculations per kg of material used are subject to substantial uncertainty. The actual amount of PEDOT in the solar cells is, however, extremely low, resulting in negligible uncertainties for the calculations for the PV cell (even at high production volumes of polymer PV systems).

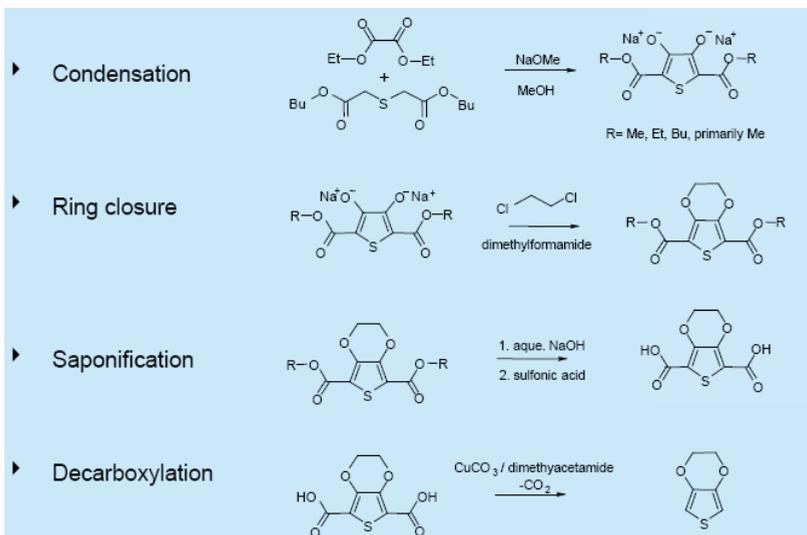


Figure 5.5: Chemical steps to produce EDOT (reproduced with permission of H.C. Starck).

The following energy and material requirements were obtained (Table 5.5 and 5.6):

Material	Amount (kg/kg PEDOT:PSS)
Propylene	0.168
Ethylene	0.224
Acetic acid	0.480
Sodium sulfate	0.568
Dichloroethane	0.244
Polystyrene	0.364
Sulfuric acid	0.700

Table 5.5: Material requirements for the production of PEDOT:PSS.

Process step	Steam (MJ/kg PEDOT:PSS)	Electricity (MJ _e /kg PEDOT:PSS)
Condensation	-	0.0481
Ring closure	6.43	0.0610
Saponification	0.105	
Decarboxylation	0.647	0.0286
Polymerisation	-	3.09
Total	6.82	3.22

Table 5.6: Energy requirements for the production of PEDOT:PSS.

Production of P3HT

For the production of P3HT, again, no process data were readily available. As we will see in the results section, even with a high environmental impact, the contribution of the photoactive layers to the total impacts is minimal, due to their extremely low thickness. This results in negligible material requirement, and, hence, negligible environmental impacts. We approximate the environmental impacts of the production of P3HT to be comparable to those of PEDOT, since they are both polythiophene derivatives and because no specifically energy intensive processes are present in the process chain leading to P3HT (checked with Fuller [40]). The impacts of PEDOT (which we used for P3HT) have been determined as part of the inventory and impact analysis of PEDOT:PSS. PEDOT:PSS contains only 28.6 % PEDOT, which is very energy intensive to produce ($NREU_{PEDOT} = 306$ MJ/kg; for comparison: $NREU_{PEDOT:PSS} = 122$ MJ/kg).

Production of PCBM

The laboratory production of PCBM is described in Hummelen et al. [41]. Industry data on energy and material use are not available and were therefore estimated by us. PCBM is produced from Buckminsterfullerene (C_{60}) and 1-phenyl-1-(3-(methoxycarbonyl)propyl) diazomethane. Especially the production of C_{60} requires a large amount of energy. Table 5.7 provides an overview of energy demand of the production of fullerene as we estimated it from various sources (these are estimates and should be dealt with with care).

Reference	Final energy or material use	Details	Primary energy (GJ _p /kg C ₆₀)
[42]	~ 129 GJ/kg C ₆₀	Solar energy	129
[43]	~ 33 GJ/kg C ₆₀	Electrical energy for plasma generator	91
[44]	~ 43 GJ/kg C ₆₀	Electrical energy for two-stage hybrid plasma generator	118
	~ 9 GJ/kg C ₆₀	Electrical energy for three-phase hybrid plasma generator	25
[45]	~ 385 kg benzene/kg C ₆₀ ~ 475 kg oxygen/kg C ₆₀	Feedstocks for fullerene synthesis in combustion	32

Table 5.7: Energy or material demand of different processes for the production of fullerene as estimated from literature.

Table 5.7 shows that there is some variation in the type of energy and the final primary energy that is needed to produce fullerene (between 25 and 129 GJ_p/kg C₆₀). For our analysis we assume the two-stage hybrid plasma generator from Bogdanov et al. [44], because it is considered to be the most cost-efficient way of fullerene production. The energy use for making fullerenes according to this process is estimated to be very high (43 GJ/kg C₆₀) and, hence, can be assumed to exceed by far the energy use of the other production steps for PCBM.

Production of lithium fluoride

For the production of LiF, no inventory data are readily available. LiF is produced from a reaction of LiOH and HF. LiOH is produced from Li₂CO₃ and Ca(OH)₂. The production of these products is well known and does not require particularly high inputs of energy. Taking into account that the LiF layer is only 1 nm thick and, hence, the material requirements are extremely small (2.6 μg/m²), we assume that the environmental impacts are negligible. We therefore do not take into account the production of LiF.

Inkjet printing

Energy use for inkjet printing was estimated from a standard office inkjet printer (HP business inkjet 2300), by letting it print a black surface (530 cm²), measuring the time (45 s) and assuming 25W-printing power (checked with technical information sheets). Electricity use is estimated to be 21.3 kJ/m².

Vacuum evaporation

The back electrode, consisting of Al and LiF, is deposited by means of electron beam evaporation. This process is described by Althaus et al. (2004) for the deposition of Titanium. Inventory data in Althaus et al. (2004) were estimated from data made available by Tinox, Germany [46]. However, according to Dr. Dasbach [47], electricity use for Al and LiF evaporation is 10-20% lower than for Titanium. Therefore we assumed 1.0 kWh/m², instead of the 1.2 kWh/m², reported by Tinox. Furthermore we accounted for the use of Al and LiF, instead of Titanium dioxide.

5.2.3.5 Multicrystalline silicon PV

Life cycle inventory data of mc-silicon PV modules have been determined and explained by De Wild - Scholten and Alsema³⁴ [9, 10], so we limit ourselves to a brief description of the production process.

A mc-silicon solar module consists of a silicon semiconductor surrounded by protective material in a metal frame. The individual solar cells are made from thin silicon wafers that are sliced from a large 240 kg multicrystalline silicon ingot. After introduction of a phosphorous dopant to form a p/n junction and deposition of an anti-reflective coating, the wafer is screen printed on one side with a fine grid of silver lines and on the other side with an aluminium/silver layer to form respectively the front and back contacts. The finished solar cells are then interconnected with copper strips and subsequently laminated between two EVA sheets, a glass front cover and a Tedlar back cover foil in order to protect it from outdoor weather conditions. The perimeter of the laminate is usually protected by an aluminium frame, although not all module types have a frame. Finally, the cables, inverter and other BOS components are added to obtain an installed system. The lifetime of modules, cables and supports is assumed to be 25 years, the inverter has a life time of 15 years.

5.2.3.6 Data sources

For estimating the environmental impacts of all materials and processes we used the data sources as listed in Table 5.8.

³⁴ Note the analyses presented in this paper are based on the LCI data set that represents the status of mc-silicon production technology of the year 2004. In the meantime an updated dataset has been published which incorporates some important improvements [48] like reduced silicon consumption and recycling of cutting fluids. For the purpose of this paper, however, these changes are less relevant.

Material/process	Details	Reference
Production of ITO coated substrate	Solar glass	[49]
	Polyethylene terephthalate	[50]
	Indium tin oxide (ITO)	[51]
	Coating: sputtering	[52]
Substrate cleaning	Deionised water	[53]
	Isopropanol	[53]
	Oxygen	[53]
	Soap	[54]
Electricity	Weighed average of 65% UCTE Electricity, 13% NORDEL Electricity, 9% CENTREL Electricity, 12% UK electricity and 1% IE electricity (All medium voltage) ³⁵	[55]
Heat	Steam, for chemical processes	[54]
Gravure printing	We used energy data of gravure printing on paper	[56]
Light fuel oil	For gravure printing	[57]
Natural gas	For lamination of flexible module	[58]
PEDOT:PSS	Propylene	[59]
	Ethylene	[50]
	Acetic acid	[53]
	Sodium sulfate	[53]
	Dichloroethane	[53]
	Polystyrene	[50]
	Sulfuric acid	[53]
Aluminium	Aluminium, liquid	[52]
Vacuum evaporating	Physical vapor deposition, using:	[52]
	- 1.0 kWh/m ² electricity (weighed average as above)	[47, 55]
	- 0.27 g/m ² Aluminium (instead of Titanium dioxide)	[52]
Lamination	We used energy data of lamination of polypropylene and paper	[60]
Ethylvinylacetate	For lamination of glass-based module	[59]
Polyvinylfluoride	Backfoil of glass-based module ³⁶	[59]
Silica gel (SiO ₂)	For lamination of flexible module	[61]
Epoxy silica nanocomposite	Hard coat of flexible module	[62] ³⁷
Epoxy resin	Adhesive for lamination of flexible module	[53]

³⁵ By using the weighed average of UCTE, NORDEL, CENTREL, UK and IE electricity, a representative mix for European electricity is obtained. (UCTE: Union for the Co-ordination of Transmission of Electricity, NORDEL: Organization for the Nordic Transmission System Operators, CENTREL: Transmission System Operators of Hungary, Czech Republic, Poland and Slovak Republic, UK: United Kingdom, IE: Ireland.)

³⁶ Due to a lack of data we used impacts of polyvinylidene chloride instead.

³⁷ In this source, inventory data are not reported as such, but were derived from process descriptions.

Alluminium alloy (AlMg ₃)	Frame	[52]
Silicone product	For diaphragma of laminator	[63]
Silicon PV module	Module, multicrystalline- silicon PV, framed	[9, 10]
BOS	Inverter	[12]
	Cables	[12]
	In-roof support structure	[12]

Table 5.8: References of materials and energy commodities used in the inventory analysis.

5.2.4 Results: Impact assessment

The impacts, as described in the goal and scope definition, were calculated for 1 W_p systems using the LCA - software SimaPro 7 [64]. The results are listed in Tables 5.9a and 5.9b. The impacts of the polymer devices seem lower than of the silicon-based devices. However, their lifetime thus far has been much shorter than of silicon-based solar cells. Consequently, more polymer devices are needed to generate the same amount of power as the silicon-based solar cell does over 25 years. In order to have equal environmental impacts as the silicon-based devices, the lifetime of polymer solar cells should be at least:

$$\text{Minimum lifetime (years)} = \left(\frac{\text{impact } 1 \text{ W}_p \text{ polymer device}}{\text{impact } 1 \text{ W}_p \text{ silicon device}} \right) \bullet 25 \text{ years}$$

Environmental impact category	Unit	Results for 1 photovoltaic device (1 W _p)		Minimum required lifetime polymer solar cells (years)
		Polymer system on substrate	PV on glass silicon PV system	
NREU	MJ	16.1	29.8	13
Climate change	g CO ₂ -eq	819	1559	13
Abiotic depletion	g Sb eq	6.63	12.5	13
Ozone layer depletion	g CFC-11-eq	0.0000468	0.000131	9
Photochemical oxidant formation	g ethylene	0.274	0.343	20
Acidification	g SO ₂ -eq	5.80	6.63	22
Eutrophication	g PO ₄ ³⁻ -eq	0.425	0.643	17

Table 5.9a: LCA results for a polymer PV system *on a glass substrate* and a silicon-based PV system, with calculation of minimum required lifetime of polymer solar cells.

Environmental impact category	Unit	Results for 1 photovoltaic device (1 W _p)		Minimum required lifetime polymer solar cells (years)
		Polymer module on flexible substrate	PV on silicon PV module	
NREU	MJ	2.35	24.9	2.4
Climate change	g CO ₂ -eq	132	1293	2.6
Abiotic depletion	g Sb eq	0.99	10.5	2.3
Ozone layer depletion	g CFC-11-eq	0.00000546	0.00012	1.1
Photochemical oxidant formation	g ethylene	0.326	0.261	31
Acidification	g SO ₂ -eq	0.97	5.09	4.8
Eutrophication	g PO ₄ ³⁻ -eq	0.058	0.54	2.7

Table 5.9b: LCA results for a polymer solar module *on a flexible substrate* and a silicon-based solar module, with calculation of minimum required lifetime of polymer solar cells.

Table 5.9a shows that, *per watt-peak*, polymer PV systems on glass substrate have lower impacts than systems based on crystalline silicon, for all impact categories. The minimum required lifetime of the polymer solar cells to break even with silicon cells is 13 years with respect to NREU, climate change and abiotic depletion. For ozone layer depletion, the minimum lifetime is shorter, i.e. 9 years, while for photochemical oxidant formation, acidification, and eutrophication, the minimum required lifetime exceeds 17 years.

Table 5.9b shows that the impacts of flexible polymer PV modules, per watt-peak, are much lower than of silicon-based modules. An exception is photochemical oxidant formation. The impacts of silicon based modules in this comparison are lower than in Table 5.9a, because no frame and BOS are assumed (in order to make a fair comparison to the flexible polymer module, which is unframed and uses no BOS either). The minimum required lifetime of the flexible module is in the order of 1 to 5 years. The reason that for photochemical oxidant formation the results are much worse for flexible polymer modules is because some toluene is evaporated during gravure printing, which has a high contribution to this environmental impact.

Tables 5.10a and 5.10b show how polymer PV systems compare to mc-silicon, thin film CdTe, thin film CIS, thin film silicon and thin film dye-sensitised PV systems for the impact categories NREU and climate change and for the energy payback time. For the calculation of the energy payback time, different sources use different assumptions on lifetime, solar irradiation, the use of a frame etc., which makes the comparison difficult. In this paper, we assumed the following data for all PV systems: medium irradiation: 1700 kWh/m²/yr, performance ratio: 0.75, and efficiency of electricity generation: 0.36 MJ_e/MJ_p. The lifetime is set to 25 years. In Table 5.10a, all modules are framed and BOS is included. In Table 5.10b no frame and BOS are used. The energy payback times for equal systems, reported by [9, 14-16] differ slightly, due to different assumptions.

The comparison shows that, per watt-peak of power output, polymer PV with glass substrate has comparable NREU and 'energy payback time' as CdTe PV (Table 5.10a). Compared to mc-silicon PV, thin film CIS PV and thin film silicon PV impacts are clearly lower. The results in this comparison are best for dye-sensitised PV, however. If we compare flexible polymer PV modules with other technologies (Table 5.10b), then the flexible module has by far the lowest environmental impacts and energy payback time. The energy payback time of the flexible module is only 0.19 years.

	Polymer (glass-based)	mc-silicon	Thin film			
			CdTe	CIS	Silicon	Dye-sensitised
NREU (MJ/W _p)	16.1	29.8	15.7	40.3	24.6	11.74
Climate change (g CO ₂ -eq/W _p)	819	1559	906	2558	1443	675
Energy payback time (yrs)	1.26	2.33	1.23	3.16	1.93	0.92

Table 5.10a: NREU, climate change and Energy payback time (under 1700 kWh m⁻² yr⁻¹ irradiation) of a polymer PV system with glass substrate compared to other solar cell technologies (all framed and with BOS). (For sources: see Table 5.1)

	Polymer (flexible)	mc-silicon	Thin film			
			CdTe	CIS	Silicon	Dye-sensitised
NREU (MJ/W _p)	2.4	24.9	9.5	34.6	17.1	5.8
Climate change (g CO ₂ -eq/W _p)	132	1293	542	2231	993	255
Energy payback time (yrs)	0.19	1.95	0.75	2.71	1.34	0.45

Table 5.10b: NREU, climate change and Energy payback time (under 1700 kWh m⁻² yr⁻¹ irradiation) of a flexible polymer PV system compared to other solar cell technologies (all unframed and without BOS).

5.2.5 Life cycle interpretation: Discussion and conclusions

From the environmental analyses conducted in this study, it appeared that the environmental impacts (per watt-peak) are much lower for the flexible PV modules on PET substrate than for polymer PV on glass substrate. One big difference is the fact that the flexible modules are not framed and assumed not to require any BOS components. Another difference is that the flexible modules are produced by a continuous roll-to-roll process which uses far less energy than the batch process used for the glass laminates. Also the deposition methods differ, i.e. on the glass-based module, the nanoscale layers are deposited by means of inkjet printing and physical vapor deposition, whereas on the flexible module, gravure printing is assumed. Cleaning and annealing are not applied in case of the flexible PV production. The production method of the flexible PV module is

based on communication with a manufacturer. The information we obtained should be representative for a flexible polymer PV production process. However, if we compare it to the production of the glass-based system, for which we obtained the data from literature, we realize that it could be oversimplified and that, in reality, environmental impacts could be higher. For example, cleaning of the ITO layer is reported to improve the efficiency and stability of the polymer solar cells, but was not mentioned by the manufacturer.

The direct comparison of flexible organic PV with glass-based organic PV is in fact rather tricky because of the different application fields and the related difference in BOS. Also the comparison of energy pay back times is awkward because the flexible cells integrated in for example an electronic device will in practice have a much lower energy production than the rigid modules which operate outdoors on a rooftop [65].

The impact assessment performed in this study is based on prospective technology for polymer solar cells, which are presently still in the laboratory stage. Therefore, the technology described in this article might differ from the technology used in the future if polymer PV systems are produced on an industrial scale. Other types of conducting polymers or different layer deposition techniques might be used. However, the technology described here serves as a good model for polymer PV systems production. As stated before, the best performing material system for application in bulk heterojunction polymer/fullerene polymer solar cells is the blend P3HT/PCBM (Section 5.2.3.1). At the moment, successful attempts are being made to improve the photovoltaic properties of conductive polymers [66, 67], which holds the possibility that in the future other, more effective polymers will be used.

We estimated the impacts for the production and the application of the layer materials. Since, however, the layers are very thin, the amount of materials is too small to contribute significantly to the final impacts. This is shown in Tables 5.11a and 5.11b, which, as an example, list the contribution of the various process steps to NREU and climate change.

Process step	Contribution to NREU		Contribution to climate change	
	MJ	%	g CO ₂ -eq	%
Solar glass production	2.49	15	114	14
ITO production	0.009	0	0.55	0
Sputtering	1.10	7	64.9	8
Substrate cleaning	0.44	3	20.7	3
PEDOT:PSS production	0.00025	0	0.0082	0
P3HT production	0.00016	0	0.0050	0
PCBM production	0.16	1	7.82	1
Inkjet printing	0.0026	0	0.13	0
Annealing	0.15	1	7.37	1
LiF production	-	0	-	0
Aluminium production	0.00096	0	0.071	0
Evaporation	0.47	3	24.0	3
Lamination	3.63	23	140	17
Framing	3.48	22	348	43
Balance of system	4.15	26	91	11
Total	16.1	100	819	100

Table 5.11a: Process contributions of a polymer PV system with glass substrate to NREU and climate change.

Process step	Contribution to NREU		Contribution to climate change	
	MJ	%	g CO ₂ -eq	%
PET substrate production	0.16	7	9.21	7
ITO production	0.009	0	0.55	0
Sputtering	1.10	47	64.9	49
PEDOT:PSS production	0.00025	0	0.0082	0
P3HT production	0.00016	0	0.0050	0
PCBM production	0.16	7	7.82	7
Gravure printing	0.054	2	3.23	2
Aluminium production	0.00096	0	0.071	0
Lamination	0.87	37	46.6	35
Total	2.35	100	132	100

Table 5.11b: Process contributions of a flexible PV module to NREU and climate change.

From Table 5.11a, we find that ITO coated glass production (production of glass and sputtering of ITO onto the glass), lamination, framing, balance of system and to a lesser extent evaporation and cleaning are the processes with a significant contribution to the

final impacts of glass-based PV. The environmental impacts of the flexible module (Table 5.11b) are mainly determined by sputtering and lamination. Of all nano-scale layers, the PCBM layer contributes most to the total impacts: around 1% in glass-based PV production and 7% in flexible PV production. This is due to the extremely high electricity use of the plasma generator. For the other layers, the contributions are by a factor 1000 lower. The uncertainties of the impacts of these layers are high to very high. However, due to their very low contribution to the total impacts, possible uncertainties can be considered to be irrelevant. The total uncertainty of the environmental assessment is mainly caused by the uncertainty of the solar glass production, sputtering, lamination, framing and BOS. Uncertainties of these processes are estimated to be 10-20%.

Toxic compounds that are released to the environment or get in contact with workers are not taken into account in this analysis. However, with proper industrial safety practices in place, risks from exposure to toxic materials are not expected either [68].

A NREU-breakdown of mc-silicon PV reveals that 72% of the energy use is related to the production of the solar cells, 12% is caused by the BOS, 5% by the frame and 4% by the solar glass (7% is others). This means that in mc-silicon PV, the photovoltaic cells have a much higher contribution to NREU than in polymer PV. The relative contributions of BOS and framing are consequently much lower. A further breakdown of NREU of the solar cells shows that electricity use is the main contributor (48%), followed by silicon carbide³⁸ (18%) and heat (14%).

For the environmental assessment, we used available LCA databases, namely Ecoinvent (see: www.ecoinvent.ch) and BUWAL 250 [56, 60]. However, it does not always contain exactly the same type of products and processes as described in the literature in the context of polymer photovoltaics. This means that the use of the datasets is sometimes an approximation of the real process and is therefore subject to some uncertainty. An example is the dataset for gravure printing, which has been derived from a dataset for printing ink on paper; another example is the dataset for lamination of the flexible module, which has been approximated from the production of a polypropylene-paper laminate. We assumed that energy use is comparable, however.

The lamination process has a large influence on the lifetime of the polymer PV module. Lamination is needed to protect the photoactive layers, but Krebs et al. [69] have shown that, with current technology, lamination reduces the lifetime of polymer solar cells. It is assumed that this is caused by the lamination procedure (with high temperature combined with mechanical stress of the cells) that damages the electrode layers. This means that for future polymer PV applications, the lamination procedure should be optimized. If the

³⁸ In a newer data set (mc-silicon production technology, status 2006, see footnote 5) internal recycling of silicon carbide and other cutting materials is included which leads to significantly lower NREU contributions from this material.

lamination procedure can be carried out at lower temperatures, this will possibly reduce the environmental impacts as well.

As we showed in this LCA, all environmental impacts (except for photochemical oxidant formation of the flexible PV module) are lower for polymer PV systems than for silicon-based PV systems. However, due to lower lifetimes of the polymer modules, more modules are needed to generate power for 25 years, which increases the environmental impacts. A break-even lifetime was estimated for the two types of polymer PV. It showed that the minimum required lifetime of polymer PV with glass substrate should be at least between 10 and 20 years and with a flexible PET substrate between 1 and 5 years. These results are particularly promising for flexible polymer PV, since lifetimes of more than one year have already been reported.

It is important to note that we have compared polymer PV (which is still in a rather early stage of development) with *present-day* production technology for crystalline silicon and thin film PV modules. These technologies will undoubtedly change over the coming years in order to reduce production costs. These changes will also affect the environmental profile of the comparison modules, and - in most cases - this change will be towards a reduced environmental impact [70]. So, as the reference technologies will improve in the coming years, polymer PV may need to improve even further than the analyses in this paper indicate.

5.3 Life cycle costing

5.3.1 Methodology

Although life cycle costing (LCC) has not yet been standardized officially at this moment, the following phases can be distinguished:

- Goal and scope definition
- Cost calculations
- Interpretation of the results

5.3.2 Goal and scope definition

In this LCC we will compare a glass-based polymer PV system with a silicon-based PV system. For the flexible module that is produced with a roll-to-roll process only very limited data are available and we consider the uncertainty too large for reporting results in this study. We limit the comparison to silicon PV since this technology is dominant on the world market. Functional unit and scope are similar to those described in the LCA part of this study.

5.3.3 Cost calculations

The cost calculations in this study have a preliminary character, due to the fact that polymer systems have not been produced on commercial scale so far. This means that costs of the materials, especially if produced on a bulk scale, are estimates and that detailed costs analyses of the manufacturing process are not possible. In Table 5.12 an overview is given of the materials and the processes that are considered in this LCC and their costs. Especially the costs of P3HT and PCBM, as listed in Table 5.12 are estimates for bulk production. In order to make costs evaluations on a system level, we have included BOS costs for a rooftop-mounted system [12].

	Costs	Unit	Source	Amount in 1 W_p of polymer PV system	Unit
Solar glass	0.0006	€/cm ²	[71]	222	cm ²
ITO sputtering costs	0.0004	€/cm ²	[72]	222	cm ²
P3HT	40	€/g	[73]	0.00056	g
PCBM	40	€/g	[73]	0.0017	g
PEDOT:PSS	Confidential	€/g	[74]	0.0022	g
Inkjet printing	0.000014	€/cm ²	Estimate ³⁹	2 x 222	cm ²
LiF	0.089	€/g	[75]	0.00006	g
Aluminum	0.0025	€/g	[76]	0.0060	g
LiF evaporation	0.0000653	€/cm ²	[47]	222	cm ²
Al evaporation	0.0000654	€/cm ²	[47]	222	cm ²
Module assembly	0.0123	€/cm ²	[77]	200	cm ²
Inverter	0.40	€/W _p	[12]	1.67 x 1 ⁴⁰	W _p
Wiring system	0.00174	€/cm ²	[12]	200	cm ²
Support system	0.00180	€/cm ²	[12]	200	cm ²

Table 5.12: Overview of unit costs.

From the values in Table 5.12, the total costs for a 1 W_p polymer PV system were calculated. The results are shown in Table 5.13.

³⁹ We used the following assumptions: investment costs for inkjet printing: € 500.000, printing rate: 0.1 m²/s, 1 fte/shift (8h), 2 shifts/day, € 72800,-/fte.

⁴⁰ We accounted for the different lifetime of the inverter (15 yrs) compared to the functional unit (25 yrs).

Material/process	Costs (€/W_p)
ITO coated glass	0.222
PEDOT:PSS	0.000
P3HT/PCBM	0.089
Inkjet printing	0.006
LiF	0.000
Aluminum	0.000
Evaporation	0.029
Module assembly	2.457
BOS	1.375
Total polymer PV system	4.178
Costs mc-silicon PV module [77]	2.500
BOS	0.935
Total mc-silicon PV system	3.435

Table 5.13: Costs of polymer PV and silicon PV.

5.3.4 Interpretation of the results

From our analysis, it appears that, per watt-peak of solar electricity output, the costs of polymer PV with glass substrate are 22% higher than the costs of silicon PV, i.e. 4.18 versus 3.44 €/W_p. The main contributors to the higher costs of polymer PV are module assembly and BOS. These elements are to a large extent area dependent (an exception is the inverter), which means that costs could be reduced if the efficiency of the solar cells increases (see section 5.4.2). The photoactive and electrode layers hardly have any significant contribution to the costs, due to the fact that the layers are so thin. The only significant costs come from the P3HT/PCBM layer, caused by a high unit price, compared to the other materials.

Unfortunately, we have not been able to run a cost calculation for the flexible polymer PV module. Since that technology uses no frame and is produced by continuous roll-to-roll processing, costs are expected to be significantly lower than of glass-based polymer PV. However, the cost calculation for polymer PV with a glass substrate gives a first indication of the economic potential of polymer PV, especially having in the back of our minds that flexible polymer PV will probably have lower costs.

5.4 Discussion

The main contributor to the costs of polymer PV with glass substrate is the module assembly. The data that we used in the cost calculations, however, originate from an analysis of mc-silicon module costs, with only an adjustment for the module area. One should realize that the cost structure for module assembly will be different for wafer-based modules and thin-film modules, especially with regard to labour costs. Unfortunately, we did not have detailed cost data for thin film modules available. In Paragraph 5.4.1 the main uncertainties of this approach are discussed.

The efficiency and the lifetime of the module determine to a large extent the outcome of the environmental and economic assessment. Therefore we further investigated these aspects. In paragraph 5.4.2 we perform a sensitivity analysis of the efficiency. In paragraph 5.4.3 a forecast is made on future costs of polymer PV if the lifetime and the efficiency are increased drastically. It is compared with future costs of mc-silicon PV.

5.4.1 Uncertainties regarding costs of module assembly

The module assembly of glass-based polymer PV differs from the module assembly of mc-silicon PV, which makes the use of similar cost data questionable. However, detailed information on the breakdown of module assembly costs for thin film modules has at present not been published. We will discuss the main uncertainties.

We estimate that about half of the costs of mc-silicon module assembly are material costs. Now, the materials used for the lamination of polymer PV are similar to those used for mc-silicon PV (i.e. glass, EVA, PVF/PET). So in that respect the data can be used for both systems. The same holds for the aluminum alloy frame.

The other 50% of the module assembly costs comprises mainly labour and equipment costs as well as some fixed costs. Here it is important to note that the assembly of mc-silicon modules involves the interconnection of 40-70 individual cells, whereas polymer solar cells are already interconnected by means of laser processing right after the active material deposition. This implies that for mc-silicon modules, labour costs are a major factor, and also some extra costs are needed for interconnection materials (copper bands, solder). For polymer PV, however, these cost items are not relevant. Moreover, if a flexible substrate is used, the equipment costs of lamination will probably be lower for polymer PV because continuous roll-to-roll lamination is applied with a higher throughput compared to mc-silicon PV, which is laminated in a batch process.

All in all, the costs that we assumed for module assembly of polymer PV will most probably be an over-estimation. An estimated 50% of the assembly costs is for labour, equipment and fixed costs, which are probably lower for polymer PV than for mc-silicon. If we assume that the real costs of polymer PV module assembly (per unit of area) are 60-

75% of the costs of mc-silicon PV module assembly, the direct manufacturing costs of polymer PV are 3.20-3.56 €/W_p (compared to 3.44 €/W_p for mc-silicon PV). This means that polymer PV could compete with mc-silicon PV on a watt-peak basis.

5.4.2 Assuming higher efficiencies

Per watt-peak, a larger area is needed for polymer PV than for silicon PV, due to the lower efficiency of polymer cells. Recently, researchers at Wake Forest University have reached a polymer solar cell efficiency of more than 6% [78]. In order to be considered a viable technology for commercial use, the cells must reach at least an efficiency of 8% [79]. It is expected that the efficiency will continue to improve and Koster et al. [80] have estimated that, ultimately, polymer solar cells can reach power conversion efficiencies approaching 11%. In Table 5.14, the effect of higher efficiencies on environmental impacts (minimum required lifetimes) and costs are presented. The calculations are done for both the glass-based devices as the flexible devices.

Minimum required lifetime (years)	Efficiency					
	Polymer PV with glass substrate			Flexible polymer PV with PET substrate		
	5%	8%	11%	5%	8%	11%
NREU	13	8	6	2.4	1.5	1.1
Climate change	13	8	6	2.6	1.6	1.2
Abiotic depletion	13	8	6	2.3	1.6	1.2
Ozone layer depletion	9	6	4	1.1	0.7	0.5
Photochemical oxidant formation	20	12	9	31	20	14
Acidification	22	14	10	4.8	3.0	2.2
Eutrophication	17	10	8	2.7	1.7	1.2
Costs (€/W _p)	4.18	2.61	1.90	No data	No data	No data

Table 5.14: Influence of increasing efficiency on environmental impacts and costs of polymer PV systems.

Table 5.14 shows that the minimum required lifetime to compete with mc-Si technology is reduced significantly by efficiency increases that seem within reach in the near future. For glass-based polymer PV, the initial minimum required lifetimes are rather high (9-22 years), due to the contribution of the glass substrate, lamination, framing and BOS. However, they are significantly reduced, down to 4 to 10 years. The results are very promising for flexible polymer PV, because the minimum required lifetimes at 11%

efficiency for NREU, climate change, abiotic depletion, ozone layer depletion and eutrophication (0.5-1.2 years) have already been reached with present day technology. At 11% efficiency the costs of glass-based polymer PV will be 1.90 €/W_p which is nearly half (55%) of the costs of mc-silicon PV with present day technology.

5.4.3 Perspectives

The economic assessment is based on cost estimates for present day technology. It is expected, though, that costs will decrease if technology matures. This holds both for polymer PV and for mc-silicon PV. If mc-silicon PV costs decrease in the future, then an even faster decrease in polymer PV costs will be required, in order to compete with mc-silicon PV. In a report by the European Communities [81], forecasts are made on the future costs of mc-silicon PV systems and polymer PV systems. An overview is given in Table 5.15.

	2013-2020	2030 and beyond	Unit
mc-silicon PV	2.5-2.0	1.0-0.5	2007 €/W _p excl. VAT
Polymer PV	0.6-0.5	<0.5	2007 €/W _p excl. VAT

Table 5.15: Predicted future costs of mc-silicon PV and polymer PV [81].

For polymer PV it is assumed that from 2013 onwards low-cost encapsulation methods are available that result in lifetimes exceeding 15 years. Furthermore it is assumed that the efficiency will be more than 10%. If this appears to be feasible, then indeed polymer PV (both glass-based and flexible) will become a cheaper and cleaner alternative to mc-silicon PV in the future.

5.5 Conclusions

The technology of polymer photovoltaics has not yet matured to large-scale industrial production and application in society. The processes we studied in this paper are based on laboratory scale technology. However, the results can be interpreted as a first exploration of environmental and economic aspects of polymer PV.

Although we initially set the functional unit for our life cycle analysis at 25 years of electricity production by a PV system with a rated power of 1 watt-peak, the actual realization of 25 years of electricity production by polymer PV would presently be difficult, because the lifetime of the cells is still low (~ one year). For this reason we first

made the comparisons on a watt-peak basis and subsequently determined the break-even lifetime for equal environmental impacts.

We have shown that, *on a watt-peak basis*, the environmental impacts are lower for polymer PV systems than for systems based on multicrystalline silicon technology. Especially for flexible modules, environmental impacts are substantially lower (the impacts are only 10-20% of silicon PV). These results are very promising. However, if the efficiency of polymer PV cells remains at its current value of about 5%, the lifetime of polymer modules should increase substantially to realize such environmental benefits (i.e. by at least ten years for polymer PV with glass substrate). Fortunately, significant improvements in life time and efficiency of polymer PV cells are indeed expected in the near future.

We also found that, per watt-peak system capacity, polymer PV has lower impacts than CIS and thin film silicon PV. Compared to CdTe systems, the environmental impacts are comparable, but dye-sensitised systems still have lower impacts.

Costs per watt-peak of glass-based polymer PV systems (at present 5% efficiency and assuming equal lifetime) appear to be about twenty percent higher than of crystalline silicon systems (4.18 €/W_p vs. 3.43 €/W_p). Unfortunately no cost data were available for the flexible PV module, but we suspect that costs will be significantly lower compared to the glass-based system. It should be noted that the costs for glass-based polymer PV in this study may well be an over-estimation of the real costs since we used data for module assembly from mc-silicon PV. For mc-silicon PV, this process involves higher labour and equipment costs than for polymer PV.

If the efficiency reaches 11% in the future, flexible modules have lower environmental impacts than silicon PV, even with present lifetime. Costs of glass-based polymer PV could drop to nearly half of the costs of present-day mc-silicon PV. On the long term, it is expected that both mc-silicon PV and polymer PV will become much cheaper to produce, with polymer PV offering clear advantages over mc-silicon PV.

At this point, we conclude that flexible polymer PV has a very high potential from an environmental point of view. Environmental impacts are considerably lower compared to silicon PV, and, if the efficiency increases, even with present day lifetime. Glass-based polymer PV potentially has environmental benefits over silicon PV if its lifetime can be increased drastically. The costs of glass-based polymer PV seem at present still too high to compete with silicon PV. Substantial R&D efforts are needed in order to increase the lifetime and efficiency of the polymer solar cells. If this is successful, both glass-based and flexible polymer PV can be very promising alternatives to crystalline silicon PV from both an environmental and an economic point of view.

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CHAPTER 6

Life cycle risks for human health: a comparison of bio-based versus petroleum-based production of 5 bulk organic chemicals

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Abstract

This paper describes the development and application of a generic approach to the comparative assessment of risks related to the production of organic chemicals by petrochemical processes versus White Biotechnology. White Biotechnology, also referred to as Industrial Biotechnology, typically uses bio-based feedstocks instead of the fossil raw materials used in the petrochemical sector. The purpose of this study was to investigate whether the production of chemicals by means of White Biotechnology has lower conventional risks than their production by petrochemical processes. Conventional risks are the risks of well-established processes, and not those related to genetically modified microorganisms and plants. Our approach combines classical risk assessment methods (largely based on toxicology), as developed by the Life Cycle Assessment (LCA) community, with statistics on technological disasters, accidents, and work-related illnesses. Moreover, it covers the *total process chain* for both petrochemical and bio-based products *from cradle to grave*.

The approach was applied to five products: the plastics PTT, PHA, PET, and PE, and ethanol. Our results show that the conventional risks related to the White Biotechnology products studied are lower than those of the petrochemical products. However, considering the uncertainties with respect to the ranges of input data, the (incomplete) coverage of emissions by the Environmental Priority Strategies (EPS) 2000 method, and the uncertainties of the assumptions made in this study (i.e., large to very large), the differences in results between bio-based and petrochemical products fall into the uncertainty range. Because of this, future research is necessary to decrease the

uncertainties before we can conclude that the conventional risks of biotechnologically produced chemicals are lower than those of fossil fuel-derived chemicals.

6.1 Introduction

Enormous progress has been made in biotechnology (including genetic engineering) in the past few years and more major scientific and technological breakthroughs are expected in the near future. In addition to the recent advances in food and animal-feed production (“Green Biotechnology”) and medical applications (“Red Biotechnology”), biotechnology is about to open new perspectives for the manufacture of organic chemicals and their intermediates. This type of technology is referred to as “White Biotechnology” or “Industrial Biotechnology” [1]. There are high expectations for White Biotechnology with regard to its usefulness for science, technology, and society in the medium to long term. Because of the (expected) risks, there is broad public resistance to Green Biotechnology in many European countries. Red Biotechnology, however, is widely accepted. It is as yet unknown how the general public will react to White Biotechnology.

In the present study, we developed and applied a generic approach to the risk assessment of the production of petrochemicals and White Biotechnology chemicals made from renewable resources (bio-based). We limited ourselves to *conventional risks*, i.e., risks of well-established processes to human health and life, taking into account accidents, illnesses, and external risks imposed on the public by emissions and technological disasters. Risks caused by genetically modified microorganisms and plants (GMO), which are probably more decisive for public acceptance, were excluded. These non-conventional risks were investigated in the BREW study [2].

This paper discusses the conventional risks of producing five organic products, namely polytrimethylene terephthalate (PTT), polyhydroxyalkanoates (PHA), polyethylene terephthalate (PET), polyethylene (PE), and ethanol. Moreover, it compares the risks related to bio-based chemical production with those of conventional petrochemical production. Our approach combines the classical risk assessment methods developed by the Life Cycle Assessment (LCA) community with statistics on technological disasters, accidents, and work-related illnesses. It was not obvious beforehand what the outcome would be because the agricultural sector (which provides the raw materials for White Biotechnology) is known for its high accident rate, while the manufacture of White Biotechnology chemicals has lower requirements for fossil feedstocks and process energy and thus lower related risks. In order to assess the total risks, the new method had to

cover the *total process chain* for both petrochemical and bio-based products *from cradle to grave*.

6.2 Methodology

This section explains the methodology that was used for the comparative risk assessment of bio-based chemicals and petrochemical products. The method is generic in the sense that it is based on risk relationships that are representative of the various steps in the process chain. In other words, it allows one to make a first estimate of the conventional risks in the total system leading to a given chemical. The process chain encompasses the entire life cycle of a chemical from “cradle” to “grave” and thus includes the following six sectors: agriculture, extraction and refining of fossil fuels, chemical industry, power generation, transport, and waste management.

Due to incomplete information, we could not consider the risks to the environment. As a result, we limited our analysis to human health risks. The total risk to human health throughout a chemical’s life cycle was estimated by summing the results of the following four risk categories:

- External risks (risks imposed on the public) due to the release of emissions from *regular* operation;
- External risks due to technological disasters;
- Risks of work-related accidents; and
- Risks of work-related illnesses.

Risk assessment was conducted as follows: for each of the four risk categories listed above, we first estimated the total risk for each of the six sectors involved (agriculture, extraction, etc.) for Western Europe as a whole. We then divided these totals by suitable reference flows (see below and second column of Table 6.2). This resulted in specific risk indicators for each sector. Since specific risk indicators could be distinguished for the various types of risks, the values for each sector could be presented in the form of a matrix. The energy, material and transport requirements in the life cycles of our products (energy and material data taken from [2]) can each be categorized into one of the sectors of the matrix and their unit can be expressed according to the reference flow of that sector. Multiplication of the life cycle input data (in TJ or tkm) by the risks of the respective reference flows of the given process chain (system) and summation of the intermediate offered a way to generically assess the overall risk. The next section explains the development of the risk matrix for each of the four categories.

6.2.1 External risks due to regular release of emissions

We based the quantification of the risks to human health on the Environmental Priority Strategies (EPS) 2000 method [3], which is a “single-score method”. “Single score” means that the various impact categories (e.g., human toxicity, climate change, acidification, etc.) are aggregated into one single indicator by means of weighting factors. The outcome is a single value for a given case. Using the EPS 2000 method, the number of ‘personyears’ lost is the common indicator chosen to measure the impact on human health. EPS methodology incorporates estimates of the hazard (damage potential) and the probability of its occurrence and is, therefore, a suitable method to express risk to human health. It distinguishes the following five categories of impact on human health:

- Life expectancy: defined as years of life lost (YOLL);
- Severe morbidity and suffering: defined as the time a human suffers severe morbidity, including starvation;
- Morbidity: defined as the time a person suffers morbidity like a cold or the flu;
- Severe nuisance: defined as a nuisance that would normally cause an evasive reaction;
- Nuisance: defined as something that is irritating, but does not cause any direct action.

The categories are all weighted differently, as can be seen in Table 6.1. Weighting factors reflect ‘willingness to pay’ to avoid the impact imposed on human health. By dividing each weighting factor by the weighting factor of the category ‘life expectancy’, we were able to express all of the categories in terms of personyears of ‘life expectancy’ (YOLL). This unit was used to quantify the risks of all inputs in this risk assessment.

Human health impact category	Weighting factor (Environmental load units ⁴¹ / personyear)	Weighting factor normalized to ‘life expectancy’
Life expectancy	85,000	1
Severe morbidity	100,000	1.1765
Morbidity	10,000	0.11765
Severe nuisance	10,000	0.11765
Nuisance	100	0.0011765

Table 6.1: Categories of impact on human health and their weighting factors according to the EPS 2000 method [3].

⁴¹ ‘Environmental load units’ were used in the EPS method to express final environmental impacts.

The risks according to EPS 2000 were calculated for each sector using the LCA tool Simapro 6 [4].

For the *agriculture sector*, 1 tonne of maize was chosen as the reference flow because grain-derived glucose is the substance most likely used in Europe in the production of chemicals by means of White Biotechnology.⁴² The risks related to the use of 1 tonne of maize, expressed in YOLL, were calculated with Simapro 6 using data from [5]. The outcome was then divided by the calorific value of the crop (14.9 GJ/tonne, see the second column in Table 6.2).

The total emissions of the ‘mineral oil and gas refineries’ in EU-15 [6] were used for the *extraction and refining of fossil fuels sector*. We used these emissions to conduct impact assessments according to EPS 2000 with the help of Simapro 6. The results of the human health risks were divided by the total crude oil consumption of the petroleum refineries in the EU in 2000 (ca. 28,200 PJ according to [7]).⁴³ The same approach was chosen for the *chemical industry sector*: total emissions from the production of ‘basic organic chemicals’ in EU-15 countries were taken from [6]. The result calculated with Simapro 6 was then divided by the total petroleum product feedstock consumption of the chemical and petrochemical industry in the EU in 2000 (ca. 2,700 PJ according to [7]).⁴⁴ For the *power generation sector*, we calculated the impact of 1 TJ of electricity using Simapro 6 (weighted electricity mix of the UCTE-, CENTREL- and NORDEL grid).⁴⁵ We also assumed that all *transport* took place with a 32-tonne load-capacity lorry. Data were from [8]. Finally, the impact of the incineration of 1 TJ of polyethylene terephthalate (PET) (HHV = 23.13 GJ/tonne) was used for the *waste management sector* (Simapro, using data from [9]). We assumed that this incineration process could be applied equally to the three other plastics (PTT, PHA, and PE) and to ethanol (for convenience, the method was applied to ethanol even though direct combustion of ethanol or its derivatives in a waste incineration plant is very unlikely due to the predominant use of ethanol as transportation fuel). Electricity and heat are produced during the incineration of PET.⁴⁶ To account for

⁴² In tropical regions, sucrose from sugar cane and vegetable oils are more likely to be the feedstocks of choice. If the technology can be successfully developed, fermentable sugar feedstocks will also be made available from lignocellulosic feedstocks such as wood.

⁴³ This value is also used to express risks due to accidents and illnesses in the next paragraphs.

⁴⁴ This value is also used to express risks due to accidents and illnesses in the next paragraphs.

⁴⁵ The categories chosen in Simapro are

- Electricity, medium voltage, production UCTE, at grid/UCTE S
- Electricity, medium voltage, production CENTREL, at grid/CENTREL S
- Electricity, medium voltage, production NORDEL, at grid/NORDEL S

The three categories were weighted according to their production shares, namely 74% UCTE, 11% CENTREL, and 15% NORDEL [16].

⁴⁶ During the incineration of 1 TJ PET, 0.106 TJ of electricity and 0.217 TJ of heat were obtained. It was assumed that the heat was obtained in the form of steam. The risks are valued negatively, however, since

the avoidance of the conventional production of electricity and heat (in the form of steam), their respective impacts (risks) were subtracted from the other risks.

6.2.2 External risks due to technological disasters

Technological disasters with fatalities appear to be relatively rare occurrences [10]. In conventional databases on disasters, no distinction is made between fatalities among employees on the production site (“on site”) and citizens outside the production site where the disaster took place [11]. As a result, it is difficult to quantify external risks due to technological disasters. [10], [12] and [13] have reported statistics on technological disasters. Based on these data, we estimated the total number of fatalities outside the production site (external fatalities) to be between 1 and 20 per year in Western Europe. As will be discussed below, this is very little compared to the impacts of the other categories.

6.2.3 Accidents

We included two types of accidents in our risk assessment: fatal accidents and accidents causing more than three days of absence from work. Several assumptions needed to be made in order to convert data on the occurrence of such accidents (data for 1999 from [14]) into YOLL. Since these assumptions are subject to substantial uncertainty, an uncertainty analysis has been included in Section 6.4.

Fatal accidents

It is necessary to estimate the number of years of life that are lost in fatal accidents. This is done by assuming the average age of the individuals who died in a fatal accident and deducting this value from the average life expectancy.⁴⁷ We found that one fatal accident was equivalent to 35 YOLL.

electricity and heat are produced instead of used. The risk from electricity production was calculated using Simapro similar as was done in the section ‘power generation’ and risk from steam using data from [17].

⁴⁷ The following assumptions/estimates were made:

- We assumed (1) that workers are employed from the age of 20 to 65 years and (2) that there is a uniform probability of a fatal accident during this period. The average age at which a fatal accident occurs then was estimated to be 42.5.
- Life expectancy for EU-15 in 2002 was 75.8 years for males and 81.6 years for females [18].
- The majority of the workers in industry is male. According to [19], 75% of the workers in manufacturing are male. This results in the average life expectancy in manufacturing to be $(0.75 \times 75.8 + 0.25 \times 81.6 =) 77.25$ years.
- A fatal accident thus reduces, on average, a life period from 77.25 years to 42.5 years. This means 34.75 years of life lost (YOLL).

Accidents >3 days absence

For accidents resulting in more than three days of absence from work, we first assumed that the EPS category ‘morbidity’ was equivalent to 0.11765 YOLL (see Table 6.1). We then estimated the average period of absence from work using another data source [15] and arrived at 30 lost working days per accident with more than 3 days of absence.⁴⁸ Finally, we concluded that one accident of this type was equivalent to 0.0136 YOLL.⁴⁹ Data on the occurrence of accidents are available for five of the six sectors⁵⁰ included in our risk analysis (data from [14]). Specific risk indicators were estimated by division by the activity level in the respective sector.⁵¹

6.2.4 Work-related illnesses

Two types of work-related illnesses (reported by [14]) were considered to be most relevant for this risk assessment: pulmonary health problems and musculoskeletal health problems.⁵² Data on the prevalence of these health problems were converted to YOLL, as discussed below.

⁴⁸ According to [15], every year nearly 5 million employees in the EU suffer from work-related accidents involving more than three days absence from work and a further 5500 are killed. In other words, 150 million workdays are lost. Due to the lack of more detailed data, we made the simplifying assumption that all workdays are lost due to accidents involving more than three days absence from work. One accident involving one employee, therefore, causes 30 lost working days (= 150 million / 5 million).

⁴⁹ With 260 working days in a year, one accident causes $30/260 = 0.115$ years of morbidity. Multiplication with a weighting factor of 0.11765 according to Table 6.1 gives a value of 0.0136 YOLL.

⁵⁰ Data on accidents are not available for waste management.

⁵¹ The following data were used as a proxy for the activity level in the various sectors:

- For agriculture, the total crop production in the EU-15 countries amounted to 4520 TJ in 1999 [20].
- For extraction and refining of fossil fuels, see text on External risks.
- For chemical industry, see text on External risks.
- For power generation, the total amount of electricity generated by electricity plants and CHP plants in EU-15 countries in the year 2000 was used as reference (9,200 PJ according to [7]).
- For transport, road freight transport (1320 Gtkm) and rail freight transport (240 Gtkm) add up to 1560 Gtkm.
- For waste management, only emission data already expressed per TJ waste were available.

⁵² We did not take into consideration the category “Stress, depression, or anxiety” [14].

Pulmonary health problems

We assumed pulmonary health problems to fall under the category ‘morbidity’ (see Table 6.1). Some occupational respiratory diseases take several decades to develop (e.g., respiratory cancer, asbestosis, and silicosis) and quite often become apparent only after retirement [14]. It was assumed, therefore, that the period of suffering from a pulmonary health problem is only 10 years. As a result, we achieved a value of 1.1765 YOLL per pulmonary health problem.

Musculoskeletal health problems

Like pulmonary health problems, we considered musculoskeletal health problems to also fall under the category ‘morbidity’. Using additional data from the United Kingdom, we were able to estimate that one case of musculoskeletal health problems represented 0.004525 YOLL.⁵³

6.2.5 Risk indicator matrix

The combination of the data discussed above led to the risk indicator matrix shown in Table 6.2, and forms the basis for the risk assessment in this study. In some cases, different sources from different years provided different data on accidents and thus resulted in a data range. Table 6.2 presents only average values.

⁵³ According to [21], there are 1.2 million work-related musculoskeletal health problems in the UK. According to [22], 12.3 million working days are lost in the UK due to musculoskeletal health problems. This means that 1 musculoskeletal health problem causes, on average, 10 working days of absence. There are 260 working days in a year, which means that 1 musculoskeletal health problem is 0.0384 personyear of ‘morbidity’. Multiplication with the conversion factor in Table 6.1 gives 0.004525 YOLL.

All values in YOLL	Reference unit	Fatal accidents	Accidents >3days absence	Musculoskeletal health problems	Pulmonary health problems	EU emissions	Total
Agriculture	1 TJ crop output	5.11E-3	1.06E-3	1.48E-4	5.01E-3	-0.0321	-0.0208
Extraction and refining of fossil fuels	1 TJ crude oil consumption	8.18E-6	7.08E-7	6.88E-7	2.47E-5	0.00716	0.00719
Chemical industry	1 TJ fossil feedstock consumption	5.72E-4	2.18E-4	8.49E-5	0.003	0.0372	0.0411
Power generation	1 TJ electricity output	1.26E-4	1.86E-5	9.19E-6	3.2E-4	0.245	0.245
Transport	1 tkm road and rail freight transport	1.11E-8	2.7E-9	2.89E-10	4.46E-9	3.48E-7	3.67E-7
Waste management	1 TJ incinerated waste	-	-	-	-	0.0517	0.0517

Table 6.2: Risk indicator matrix in ‘years of life lost’ (YOLL) expressed per reference unit.

6.3 Results

Applying the risk assessment method described above to the chosen cases resulted in estimates for the total number of years lost per unit of product throughout the process chain. The final results are shown in Table 6.3 for PTT, PHA, PET, PE, and ethanol. Since both petrochemical and bio-based production routes exist for PTT and ethanol, we were able to compare the risks between bio-based and petrochemically derived products. PHA is only produced with bio-based feedstocks, while PET and PE are petrochemical alternatives. Therefore, we compared (bio-based) PHA to (petrochemical) PET and PE. The results are shown graphically in Figures 6.1-6.6, distinguishing between the types of risks and the sectors in which the risks occur.

According to the results shown in Figures 6.1-6.6, the conventional risks of all bio-based products are lower than those of the petrochemical products. For example, the total risk of bio-based PTT is 12-25% lower than that of petrochemical PTT. The risk caused by the production of PHA by fermentation is 7-22% lower than that caused by the production of petrochemical PET and 39-49% lower than that of petrochemical PE. The

risk caused by the production of ethanol by dry milling is 68-74% lower than its production from ethylene. While these results seem to justify the conclusion that the risks related to bio-based products are lower than those for petrochemical products, the uncertainties of the method must be taken into account before drawing final conclusions. An uncertainty analysis, therefore, is presented in Section 6.4 (see below).

As Figures 6.1 and 6.3 show, by far the most important types of risks (expressed as YOLL) are the external risks due to the regular release of emissions to the atmosphere, followed by pulmonary health problems of the workforce and accidents of the workforce (fatal accidents and accidents resulting in more than three days of absence). External risks imposed on the public due to technological disasters are negligible.

The results allowed us to compare the distributions of the risks over the risk categories and the industrial activities. We were able to draw the following conclusions. (1) The largest difference between bio-based and petrochemical products concerns the risks related to the regular release of emissions to the atmosphere. (2) Pulmonary health problems and fatal accidents tend to be more important in the production of bio-based polymers than petrochemical products, but these differences are by far outweighed by the risks caused by the regular release of emissions to the atmosphere. (3) The breakdown of the total risk by sector shows that the chemical industry is more important for the petrochemical products than for bio-based products. (4) Waste management is equal or very similar for all production routes (petrochemical and bio-based) because it is based on the calorific value of the product (the production method had no influence). (5) Transport is equal for bio-based and petrochemical production because the same transport was assumed for all production routes (500 tonne-km by 32-tonne load-capacity lorry). (6) The agriculture sector is only relevant for bio-based production routes. The cultivation of crops yielded a “negative risk” in the agriculture sector, because of the uptake by crops of CO₂ from the air (CO₂ uptake is valued as a negative impact by the EPS 2000 method). (7) The share of the extraction and refining of fossil fuels sector tends to be slightly higher for petrochemical production routes. (8) The power generation sector has a similar share in both the bio-based and petrochemical production of PTT. Compared to PET and PE, the share is higher for the production of PHA. With regard to the production of ethanol, the share of the power generation sector is very small to negligible in all cases.

Product	Risk (YOLL/tonne product)
PTT ⁵⁴	
- from ethylene oxide	0.003821
- from acrolein	0.004031
- via anaerobic fermentation on dextrose	0.003001
- via anaerobic fermentation on glycerol	0.003227
- via aerobic fermentation 1	0.003039
- via aerobic fermentation 2	0.003381
PHA ⁵⁵	
- via fermentation 1	0.002501
- via fermentation 2	0.002988
PET ⁵⁶	0.003211
PE	0.004949
Ethanol ⁵⁷	
- from ethylene	0.003535
- via maize dry milling 1 (low estimate)	0.000934
- via maize dry milling 2 (high estimate)	0.001114

Table 6.3: Results of the risk assessment for PTT, PHA, PET, PE, and ethanol.

⁵⁴ PTT from ethylene oxide and acrolein is derived petrochemically. PTT via fermentation is bio-based. Two datasets were available for the aerobic fermentation process. They are called Aer 1 and Aer 2 in Figures 6.1 and 6.2.

⁵⁵ PHA is derived only via fermentation. This is bio-based. Two datasets were available for the fermentation process. They are called PHA 1 (from glucose) and PHA 2 (from glycerol) in Figures 6.3 and 6.4.

⁵⁶ PET and PE are derived petrochemically.

⁵⁷ Ethanol from ethylene is derived petrochemically. Ethanol via maize dry milling is bio-based. Two datasets were available for the dry milling process. They are called dry milling 1 and dry milling 2 in Figures 6.5 and 6.6.

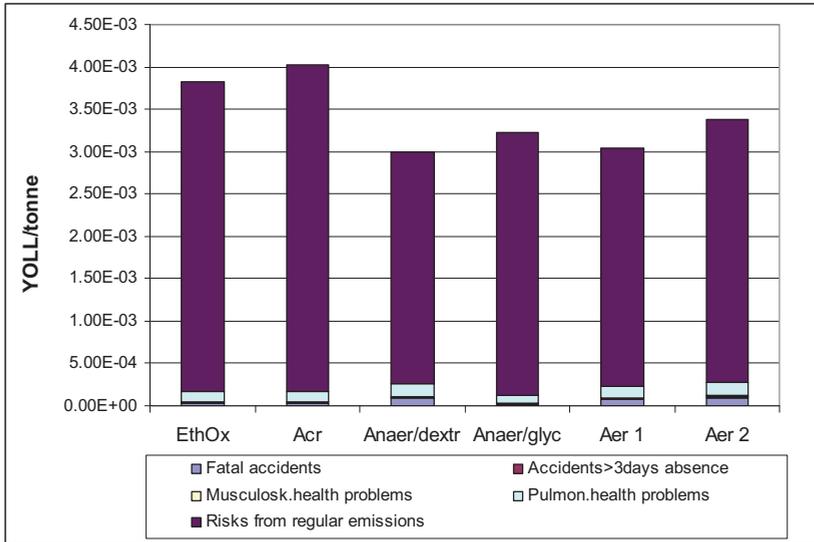


Figure 6.1: Risk for 1 tonne of PTT per risk category (abbreviations: compare Table 6.3).

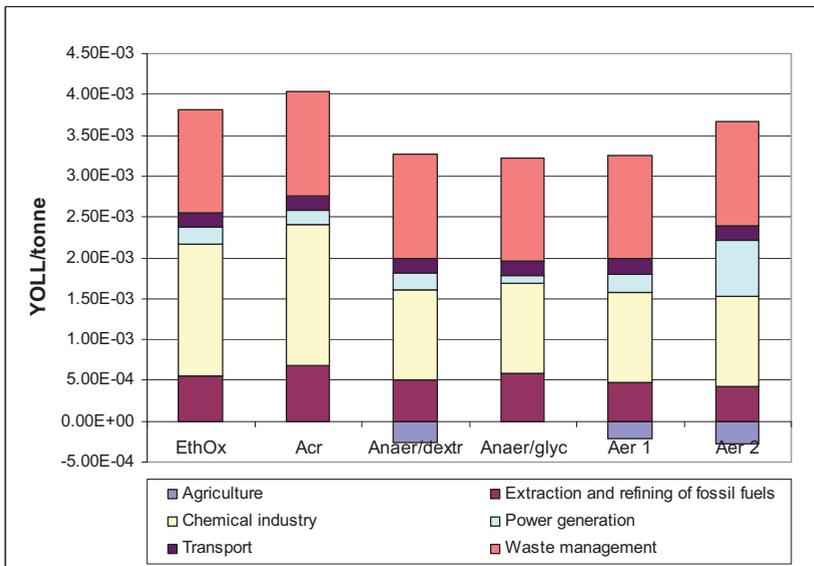


Figure 6.2: Risk for 1 tonne of PTT per sector.

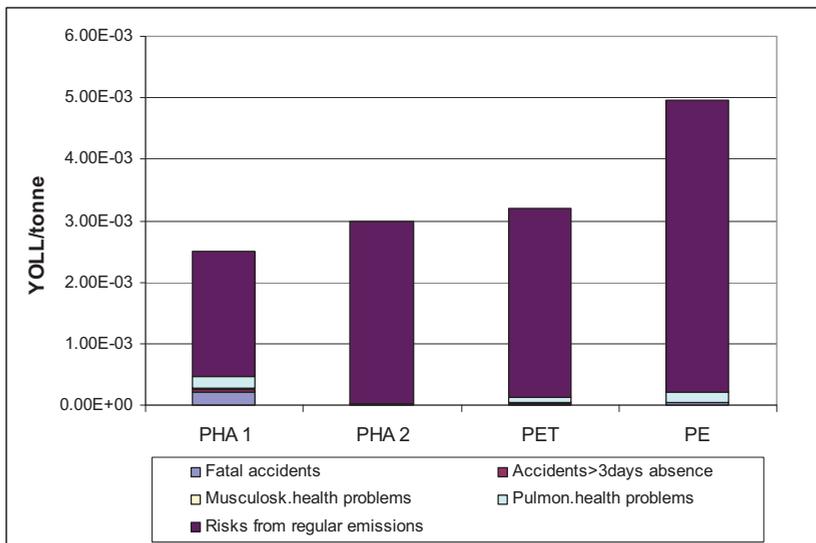


Figure 6.3: Risk for 1 tonne of PHA, PET, and PE per risk category.

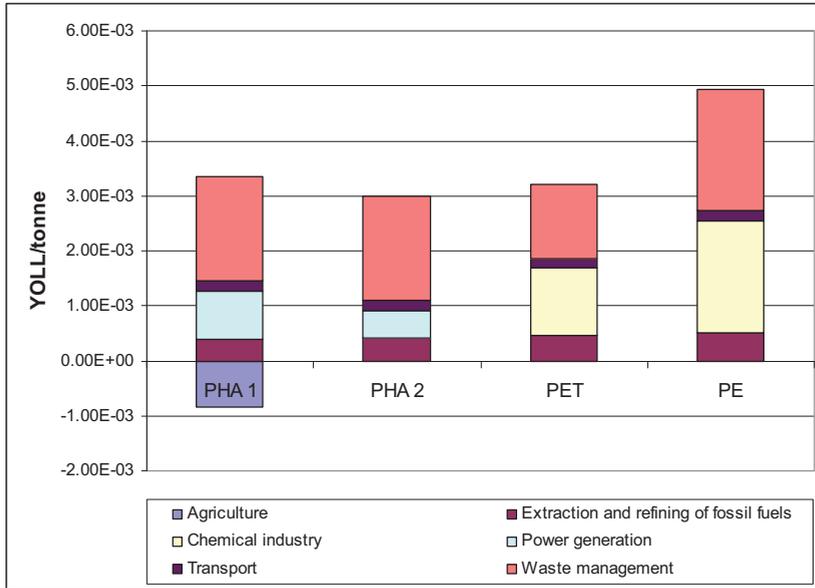


Figure 6.4: Risk for 1 tonne of PHA, PET, and PE per sector

Note:

- PHA 1 is produced from glucose, while PHA 2 is produced from glycerol, which is considered a “waste product” (from biodiesel production). For this reason, none of the impacts related to agriculture were allocated to glycerol.

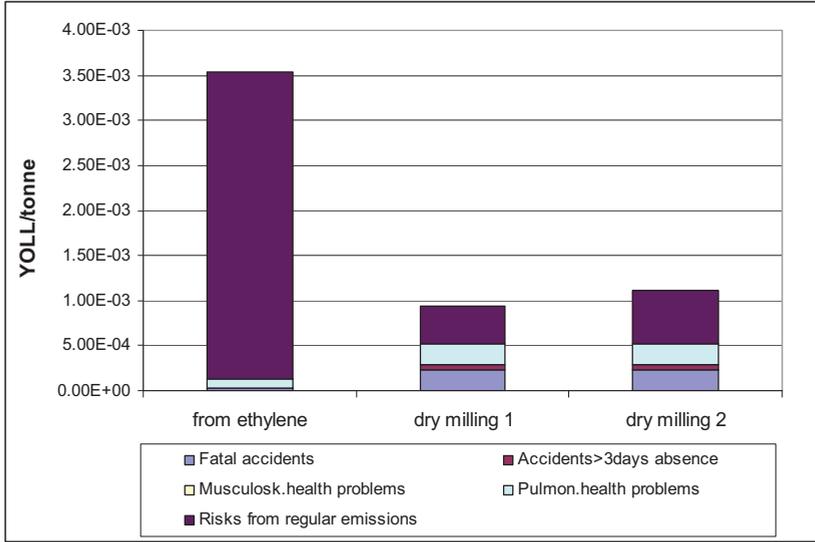


Figure 6.5: Risk for 1 tonne of ethanol per risk category.

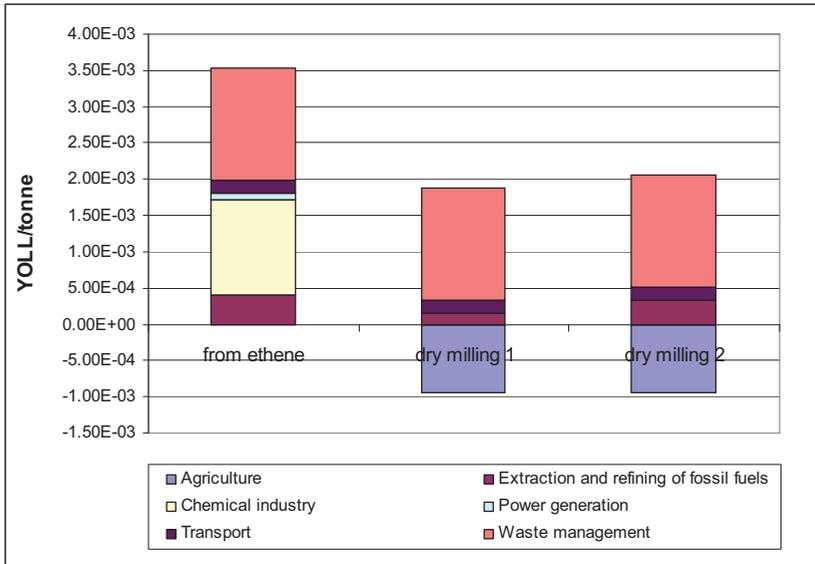


Figure 6.6: Risk for 1 tonne of ethanol per sector.

6.4 Uncertainties

In order to assess the quality of our results, we conducted an uncertainty analysis comprising the following factors:

- Ranges of input data (only for accidents; no range was found for the other risk categories);
- Uncertainty analysis for accidents and illnesses;
- Coverage of emissions in the SimaPro impact assessment (not all emissions are defined by the EPS 2000 method); and
- Checking the plausibility of the results by comparing them with values taken from other literature sources

6.4.1 Ranges of input data

The data sources reported different values for accidents. The ranges are shown in Table 6.4; the uncertainties ranged from 0% to 44%.

	Fatal accidents	Range (around arithmetic mean value)	Accidents > 3days absence	Range (around arithmetic mean value)
Agriculture	1.47E-4 #/TJ	± 3%	0.0777 #/TJ	± 3%
Extraction and refining of fossil fuels	2.36E-7 #/TJ	± 25%	No range	± 0%
Chemical industry	1.65 E-5 #/TJ	± 28%	No range	± 0%
Power generation	3.61E-6 #/TJ _e	± 1%	0.00137 #/TJ	± 10%
Transport	3.19E-10 #/tkm	± 31%	1.99E-7 #/TJ	± 44%

Table 6.4: Data ranges for fatal accidents and accidents with >3 days of absence

6.4.2 Uncertainty analysis for accidents and illnesses

The conversion of accidents and health problems to YOLL is based on assumptions concerning the time period in which a person suffers. This time period can be crucial for the results.

- As explained above (Section 6.2.3), a fatal accident is assumed to reduce a life, on average, by 35 years. We estimated the uncertainty of this assumption to be ±10

- years. When the risk due to fatal accidents (see Table 6.2) was recalculated using this ± 10 -year range, the uncertainty range of this type of risk is $\pm 29\%$.
- The average period of absence for accidents causing >3 days of absence from work was considered to be 30 days. When an uncertainty of ± 10 days is assumed, the uncertainty for this type of risk is $\pm 33\%$.
 - The assumptions for pulmonary health problems are very rough. We assumed a maximum of 10 years of suffering morbidity. When this period is shortened by five years or extended to 35 years (the assumed number of years lost due to a fatal accident), the range of uncertainty becomes roughly -50% to $+150\%$.
 - A 10-day absence was assumed for each musculoskeletal health problem. When an uncertainty of ± 5 days is assumed, the risk uncertainty becomes $\pm 50\%$.

We found that the contribution of the emissions of 'Ethanol-dry milling 1' to the total risk is the lowest compared to the other cases tested. The contribution of the other risk categories is therefore highest. When the uncertainties listed above were applied, an overall maximum uncertainty of the assumptions was obtained (for the other cases - PTT, PHA, PET, PE, and Ethanol-dry milling 2 - the contributions of accidents and illnesses to the final result are lower, thus the overall uncertainty of the final risk due to the assumptions is also lower than for Ethanol-dry milling 1). Recalculation of the final risk using the uncertainty ranges identified above resulted in a lower risk value of 0.000730 YOLL/tonne and an upper risk value of 0.001369 YOLL/tonne (original value was 0.000934 YOLL/tonne). This means that the maximum uncertainty of the results for all cases is -22% and $+47\%$. In conclusion, the uncertainty range for accidents and illnesses is rather limited and the final result for total risk remains within the same order of magnitude (only for ethanol does the risk pattern change somewhat; emissions remain the dominant risk source for all other cases).

6.4.3 Coverage of emissions by EPS 2000

The emissions impact for each of the six sectors in this risk assessment was determined using the EPS 2000 method in SimaPro 6. Relatively few types of emissions, however, could be defined using this method (11-32%, see Table 6.5) and no impact results were calculated for the other types. As a result, the impact determined using the EPS method represents an underestimation of the real impact.

Sector	Impacts based on:	Fraction of emissions defined in EPS 2000 ⁵⁸
Agriculture	Grain maize IP, at farm	11%
Extraction and refining of fossil fuels	EU-15 emissions ‘mineral oil and gas refineries’	32%
Chemical industry	EU-15 emissions ‘basic organic chemicals’	28%
Power generation	CENTREL/NORDEL/UCTE medium voltage electricity mix, at grid	11%
Transport	Transport, lorry 32 t	11%
Waste management	Disposal, polyethylene terephthalate, 0.2% water, to municipal incineration	11%

Table 6.5: Coverage of emissions by EPS 2000.

6.4.4 Plausibility check by comparison with other literature data

In order to assess whether our results for PTT, PHA, PET, and PE are plausible, we compared our work with the scarce results found in literature. The method of comparison we used is as follows:

If we make the simplifying assumption that the plastics studied in this paper are quite representative for plastics (and their production) in general, then the total risk (expressed in YOLL) can be calculated using the (average) results in Table 6.3. When the total risk (in YOLL) of all industrial sectors is known, the share of the plastics sector can be calculated. To check the plausibility of the outcome, this value is compared to the value of the plastic industry’s share of the total primary energy supply (TPES) in Europe.

In Europe, the current average production of plastic per capita is 145 kg (55 Mtonne plastic produced annually divided by 380 million inhabitants). A total of 145 kg plastic per capita can be translated to YOLL using the results of our research. Assuming that all plastics consist of PTT, PHA, PET, or PE, the average risk of 145 kg plastic per capita is 0.5 YOLL/1000 persons. The total impact of all emissions of all sectors in Europe in 2001 was estimated by [6] to be 6.24 YOLL/1000 persons. The share of plastic then is 0.5/6.24, i.e., 8%.

⁵⁸ This was calculated as the number of substances defined by EPS 2000 divided by the number of substances for which emissions data were available. It was NOT based on the absolute amounts of emissions. For the agriculture, power generation, transport, and waste management sectors, coverage was 63 out of 552 substances. The coverage was 16 out of 50 substances for the extraction and refining of fossil fuels sector and 16 out of 57 substances for the chemical industry sector.

Plastics are produced by the chemical industry. The primary energy consumption by the chemical and petrochemical industry can be estimated (149 Mtoe) using energy data published by [7]. The total primary energy supply (TPES) in 2000 was 1460 Mtoe. This means that the primary energy use by the European chemical and petrochemical industry was 10% of the total TPES. This is consistent with the 8% derived above.

6.5 Conclusions

This paper describes the successful development and application of a method of generic risk assessment that covers the total process chain of petrochemical and bio-based products from cradle to grave. It focuses on the conventional risks to human health, taking into account accidents, illnesses, and external risks imposed on the public due to emissions and technological disasters. Risks related to genetically modified microorganisms and plants (GMO) are excluded.

As by far the most important sources of risks (expressed as YOLL) we identified the external risks caused by the regular release of emissions into the atmosphere, followed by pulmonary health problems of the workforce and accidents of the workforce (fatal accidents and accidents causing more than three days of absence from work). External risks imposed on the public due to technological disasters were found to be negligible.

Our results showed that the chemical industry sector contributed more to the final risks of petrochemical products than bio-based products and that the agriculture sector was only of relevance to bio-based products.

We found that the conventional risks are lower for bio-based products than for petrochemical products. This result is partly driven by the lower energy use in the life cycle of the bio-based products because they are produced from bio-based feedstocks and by the fact that bio-based feedstocks take up carbon from the air. Taking into account the uncertainties with respect to the ranges of input data, the (incomplete) coverage of the emissions by EPS 2000, and the uncertainties of the assumptions made in this study (large to very large), the differences in the results between bio-based and petrochemical products (in favor of bio-based production), however, fall into the uncertainty range. This means that we cannot conclude without due consideration that conventional risks of biotechnologically produced chemicals are lower than those of chemicals derived from fossil fuels. We can suspect that conventional risks are lower for the bio-based chemicals but further research, especially with better data, will have to be conducted in order to decrease the uncertainties so as to make a firm statement on this issue.

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CHAPTER 7

Conclusions

In the past, new technologies have opened new perspectives for society, but sometimes were also accompanied by unforeseen risks to human health or to the environment. To reduce the risk of unforeseen consequences, early (i.e. 'ex-ante') assessments of chances and risks of new technologies are required. Nanotechnology and white biotechnology are emerging technologies with huge potentials. However, in order to assess their viability (and account for potential risks) compared to conventional technologies, the technologies have to be assessed in an early stage.

In this thesis, the chances and risks of nanotechnology and white biotechnology have been studied ex-ante. First, the environmental impacts and costs of polymer nanocomposites and polymer photovoltaics have been assessed. Next, the risks to human health of PTT, PHA and ethanol (all white biotechnology chemicals) were determined. Through these case studies, this thesis contributes to an improvement and extension of the existing methodology of life cycle engineering to allow a more comprehensive ex-ante assessment. The methodological contributions will first be discussed (paragraph 7.1). Next, the main conclusions of the ex-ante assessments of nanotechnology (paragraph 7.2) and white biotechnology (paragraph 7.3) are discussed.

7.1 Improvements and extensions to the existing LCE methodology

The analyses in this thesis involve comparisons of the products of new technologies (i.e. nanotechnology, white biotechnology) with existing technologies. The nanotechnology products, i.e. polymer nanocomposites and polymer photovoltaics, are to a large extent still in the laboratory stage. It is therefore a challenge to extrapolate laboratory-scale data to estimate performance for industrial practice. This was successfully achieved by combining inventory data on material use, energy use and required processes (e.g. extrusion, spray drying, chemical vapour deposition) as obtained from laboratory technology with data on large-scale industrial practice. Once a realistic set of material

and energy requirements had been established, an environmental impact assessment could be performed.

For example, a polypropylene nanocomposite is produced from nanoclay and polypropylene in a pilot plant at the Institute for Polymer Research (IPF, Dresden, Germany). Information on the process steps leading to the nanocomposite was obtained from this institute. The data obtained from IPF (such as the amount of material to be extruded) were combined with energy and material data as found for industrial scale processes (e.g. an industrial extruder) to arrive at an estimate for large-scale industrial practice. A similar approach was taken in the study on polymer photovoltaics (Chapter 5). Only laboratory data were available and an estimate for real industrial practice was made in this thesis. This was done by contacting manufacturers, such as for PEDOT:PSS (a hole-conducting polymer layer) or by searching publicly available literature, such as for PCBM (together with P3HT responsible for the generation of an electric current under influence of light). A similar procedure was followed for the required processes for the fabrication of the solar cells. First, a decision had to be made about representative processes (e.g. the deposition techniques and the process for lamination), next energy and material requirements had to be estimated for industrial practice.

Another problem that occurs with estimating material requirements is when a new, laboratory stage material is compared with a well established material for the same functional unit, such as the packaging film, the greenhouse film and the car panels in Chapter 2. For the well established materials it is normally well known how much material is used. However, for the same product from the novel material this has often not yet been determined. In this case, the Ashby material indices have been used (see Chapters 2 and 3) as quantitative metric of the material properties, thereby allowing to establish the material requirements. The higher the Ashby material index, the better the mechanical properties and the less material is needed for the same function. The material requirements are therefore inversely proportional to the material index:

$$\frac{\text{Material requirement product A}}{\text{Material requirement product B}} = \frac{\text{Material index product B}}{\text{Material index product A}}$$

It should be noted that this approach focuses only on mechanical properties (while there are many further features, such as fire-retardancy or durability) and it is an estimate based on very generic assumptions. These assumptions concern the exact functionality to be chosen (e.g. panel, tie, beam, shaft etc.) and, hence, the required material properties involved (e.g. Young's modulus, tensile strength and/or density). Different choices could seriously change the outcome of the assessments. While involving uncertainties, it allows

making first estimates for the assessment of novel materials compared to conventional materials. This approach was also followed in Chapter 3, where the ‘functionality-based non-renewable energy use (NREU)’ was determined, based on the ratio of the NREU (per kg) and the Ashby material index. By taking this ratio, it accounts for differences in energy use (e.g. as a result of extra process steps required to produce nanoobjects and mix them in a polymer matrix) and accounts for differences in mechanical properties. This functionality-based NREU, as an indicator is similar to the approach for the comparative assessment used in Chapter 2 (as it accounts for changed impacts of production and differences in mechanical properties). It can be applied to any nanocomposite and allows comparing nanocomposites with different polymer matrices and/or with different loads of nanoobject-filler (such as in Chapter 3).

The new approaches concerned mainly assessments of energy and material requirements of novel products. In contrast, in Chapter 6 a new impact assessment approach was developed, i.e. an extension of the expression of risks to human health based on a life cycle perspective. In this approach, the weighting factors of the Environmental Priorities Strategy (EPS) 2000 method on ‘life expectancy’, ‘severe morbidity’, ‘morbidity’, ‘severe nuisance’ and ‘nuisance’ (all human health impacts categories) have been used to convert all categories to one single indicator, i.e. ‘life expectancy’ with the unit ‘years of life lost (YOLL)’ (see Chapter 6). Conventional life cycle impact assessments normally assume regular operations for the calculation of environmental impacts. We follow the same approach but we extend the methodology by also accounting for risks of technological disasters, work-related illness (i.e. musculoskeletal health problems and pulmonary health problems) and work-related accidents (i.e. accidents causing more than three days absence, and fatal accidents). We developed a generic methodology, by defining reference units for each of the six economic sectors involved in the process chain. For each of these reference units, the total risk (expressed in YOLL) was determined based on public literature regarding the risk categories just mentioned and own assumptions (see Chapter 6). Next, the total risks per unit of product was determined.

The described methodology developed in this thesis was successfully applied to the life cycles of PTT, PHA, PET, PE and ethanol. The results seem to favour bio-based chemicals. However, the uncertainties are high. Therefore, the main insight gained was on the development and applicability of the methodology. Further efforts are required to improve the quality of the data used.

7.2 Nanotechnology

In this thesis, ex-ante assessments have been performed for two nanotechnology-based products, i.e. polymer nanocomposites and polymer photovoltaics.

Chapter 2 introduced the use of Ashby's material indices to estimate material requirements. It was applied to the use of a polypropylene nanocomposite for packaging film, agricultural film and car panels. The conventional materials were pure polypropylene for the use in packaging film, pure low-density polyethylene (LDPE) for the use in agricultural film and glass fibre-reinforced polypropylene for the use in car panels. For each of the applications a comparative environmental assessment was performed. Clear environmental benefits were observed only compared to pure low-density polyethylene used in the agricultural film, the main reason being the much better mechanical properties of the polypropylene nanocomposite compared to pure LDPE. As a result, weight savings were highest for the use as agricultural film. For the application of the polypropylene nanocomposite in packaging film and car panels the environmental impacts are similar for the nanocomposite material and the conventional material.

Chapter 2 also contains an economic assessment of the polypropylene nanocomposite for each of the different applications (using the LCC methodology). A problem that arose was that prices of the input materials and energy carriers vary over the years and differ per source. Therefore a low and a high estimate were calculated for the economic performance of the polypropylene nanocomposite. It appeared that in most of the cases studied, there were economic benefits for the polypropylene nanocomposite. However, the price of nanoclay is uncertain (range of 4400 – 10000 € / tonne). It was found that at a maximum nanoclay price of around 5000 € / tonne, the polypropylene nanocomposite material offers economic advantages for the application in packaging film, agricultural film and automotive panels.

In Chapter 3, the effect of using nanoobjects as reinforcing filler on the functionality-based NREU of nanocomposites was investigated. The functionality-based NREU is an indicator that simultaneously addresses environmental impacts (represented by the NREU) and mechanical impacts (represented by the Ashby material indices for the functionalities 'panel' and 'tie'). Twenty-three different nanocomposites were studied. For 18 of these, the study showed benefits for the nano-reinforcement of polymers. We draw the conclusion that the use of nanoobjects for reinforcement of nanocomposites can be beneficial from an environmental point of view.

It should be noted that in the comparison of the polypropylene nanocomposite with pure polypropylene (used for packaging film in Chapter 2) there is a small difference with the analysis in Chapter 3, because in Chapter 3 the functionality ‘panel’ is assumed, while in Chapter 2 the functionality ‘tie’ is assumed. For the comparison with the glass fibre-reinforced polypropylene (used for car panels), the use phase has been taken into account in Chapter 2, with a large fuel consumption allocated to the car panels, while in Chapter 3 stationary use is assumed. As a consequence, the analyses show slightly different results being to the disadvantage of the polypropylene nanocomposite in Chapter 3.

If nanocomposites are incinerated, there is a risk of possibly toxic nanoobject emissions into the environment due to incomplete cleaning of the off-gases. This might become a serious problem if nanocomposites will be used on a large scale and when the amount of nanoobjects in the waste increases. It appears that many primary and secondary nanoobjects arise from the incineration of nanoobjects in the grate incinerator. An analysis of the off-gas treatment section showed that for objects smaller than 100 nm, removal from the off-gas might not be sufficient and they are possibly emitted into the environment. Nanoobjects that are removed, however, will end up in the solid residues. Since solid residues are usually landfilled or used as construction material, leaching of nanoobjects into the environment should be prevented. Further research is recommended to reveal the real risks to human health and the environment. Laboratory experiments on the fate of nanoobjects in the grate incinerators and during off-gas treatment are proposed, as well as more *in vivo* tests on the toxicity of nanoobjects.

Apart from nanocomposites, another product of nanotechnology has been evaluated in an early stage, i.e. a polymer photovoltaic (PV) system. Polymer PV cells consist of a substrate (could be glass or flexible) onto which semi-conducting conjugated polymer layers are deposited that convert light to electricity. These layers have a thickness of typically 100 nm. An environmental assessment was conducted for a system on a glass substrate and a flexible module on a PET substrate. An economic assessment has been conducted only for the system on a glass substrate (due to a lack of reliable data for the flexible system). The polymer PV system was compared to a multicrystalline (mc)-silicon PV system. Since the power generation efficiencies of polymer PV and mc-silicon PV are different (5.0 and 13.2 % respectively) the areas per watt-peak of output power also differ. If measured per watt-peak, the environmental impacts compared to a mc-silicon PV system are 20–60% lower for polymer PV systems with glass substrate and 80–95% lower for polymer PV with PET as substrate (flexible modules). However, the lifetime of the polymer PV cells is at present much lower compared to mc-silicon PV cells (i.e. around one year for polymer PV compared to 25-30 years for mc-silicon PV). This means that a comparison only based on a watt-peak device is not fair because the two systems

are incomparable due to the different lifetimes. Therefore, the minimum required lifetime was estimated for polymer PV systems to have equal environmental impacts as the mc-silicon PV system. For polymer PV on a glass substrate the minimum required lifetime is around 10-20 years. For flexible polymer PV it is roughly 1-5 years (an exception is photochemical oxidant formation; for this impact it is 31 years). Also a comparison has been made with other solar cell technologies. Polymer PV with a glass substrate has shown to have comparable environmental impacts as CdTe thin film PV. It has lower impacts than CIS and silicon thin film PV. Dye-sensitised PV has lowest impacts, however. A flexible polymer PV system has by far lowest impacts compared to all other types of PV. The costs of a polymer PV system (on glass) are approximately 20% higher than a mc-silicon PV system. However, since most of the costs are area dependent (such as for balance-of-system and module assembly) an increase in efficiency (and, hence, a reduction of the area per watt-peak) would lower the costs. Therefore, the main challenge in polymer PV technology is to increase the lifetime on the one hand and the efficiency on the other hand.

The studies presented in this thesis have shown promising results for nanotechnology. Most nanocomposites show environmental benefits compared to pure polymers. The polypropylene nanocomposite also shows cost benefits. Polymer PV has the potential to become an environmentally friendly and cheap alternative to mc-silicon PV, provided that the lifetime and efficiency are increased. But there are also risks: the incineration of nanocomposites can result in nanoobject emissions that might be toxic to humans and to the environment. Further research is required.

7.3 White biotechnology

As a next step, potential risks of white biotechnology were studied. A methodology for generic risk assessment was developed based on conventional risks (i.e. risks of well established processes, excluding e.g. risks of genetically modified organisms) to human health for each of the industrial subsectors involved, i.e. agriculture, extraction and refining of fossil fuels, chemical industry, power generation, the transport sector and waste management. The estimated risks are expressed in ‘years of life lost (YOLL)’ being a measure for the amount of years an average person loses in his life due to the production of a product. The risk assessment was applied to PTT, PHA, PE, PET and ethanol, thereby assessing bio-based versus petrochemical production (for PTT and ethanol both bio-based and petrochemical processes are compared, whereas bio-based PHA is compared to petrochemical PET and PE). It appeared that the conventional risks

of all bio-based products are lower than those of the petrochemical products. Besides, the analysis revealed several insights. We summarize the most important ones:

- The largest difference between bio-based and petrochemical products concerns the risks related to the release of emissions to the atmosphere.
- Pulmonary health problems and fatal accidents tend to be more important in the production of bio-based polymers than petrochemical products, but these differences are by far outweighed by the risks caused by the release of emissions to the atmosphere.
- The breakdown of the total risk by sector shows that the risks caused by the chemical industry have a larger share for the petrochemical products than for bio-based products.
- The risks related to waste management are equal or very similar for all production routes (petrochemical and bio-based) because they are based on the calorific value of the product (the production method had no influence).
- The agricultural sector is only relevant for bio-based production routes.

Although, based on the analysis in this thesis, the conclusion seems justified that the chemicals produced with white biotechnology have lower risks compared to the chemicals produced petrochemically, the uncertainties are considerable. Therefore, in order to support this conclusion, further research is required, especially with better data that would reduce the uncertainty.

Ex-ante analyses have successfully been applied in this thesis to nanotechnology- and white biotechnology-based products. The methodology has been improved and extended. The Ashby method has proven to be a good tool for assessing material requirements of novel materials. Furthermore, it has been shown how data for industrial practice can be estimated from lab data. These contributions concern first steps, however, and leave further room for improvement of the approaches taken. Based on the assessments in this thesis we find promising opportunities for nanotechnology and white biotechnology. According to the analyses performed in this thesis these technologies can contribute to a more sustainable society. However, negative side-effects need to be carefully monitored and suitable measures must be taken to minimize them. In order to strengthen the conclusions and to further improve the methodology on ex-ante assessments, we propose further research. Especially the translation from lab-scale data to a reliable estimate for industrial practice should be studied more extensively. Furthermore, experiments should be conducted to determine the exact fate of nanoobjects in the waste incineration process and their impacts.

Samenvatting in het Nederlands

Wetenschappelijk onderzoek en nieuwe technologieën hebben voor enorme vooruitgang gezorgd in de maatschappij. Technologische uitvindingen hebben de basis gelegd voor de moderne wereld zoals we die nu kennen. Centraal daarin staat de productie van nieuwe, geavanceerde materialen. Er worden voortdurend nieuwe technologieën ontwikkeld, zoals bijvoorbeeld nanotechnologie, industriële – of ‘witte’- biotechnologie, metamaterialen technologie, quantum dots, supergeleiding bij hoge temperatuur, programmeerbare materialen en zichzelf reparerende materialen.

Hoewel nieuwe technologieën voor enorme vooruitgang hebben gezorgd, zijn er ook schaduwkanten: De schaal van industrialisering is enorm en de aarde blijkt hier zwaar onder te lijden te hebben. Grote mondiale milieuproblemen zijn het gevolg. Een aantal materialen heeft in het bijzonder veel schade aangericht aan mens of natuur. Voorbeelden zijn benzeen, asbest, gesubstitueerde bifenylen (‘polychlorinated biphenyls – PCBs’), halonen, tributyltin en dichlorodiphenyltrichloroethaan (DDT).

Om schadelijke gevolgen van materialen of technologieën in kaart te brengen, moeten deze systematisch beoordeeld worden op hun effecten. Het analyseren en evalueren van gevolgen, kansen en risico’s van nieuwe en bestaande technologieën wordt ‘technologie beoordeling’ genoemd. Bij de zojuist genoemde materialen kwamen de schadelijke gevolgen pas naar boven nadat ze al op grote schaal werden gebruikt. Het is daarom van groot belang dat nieuwe technologieën worden beoordeeld vóórdat ze zijn toegelaten op de markt. Het gezichtspunt moet ‘ex-ante’ zijn (d.w.z. toekomstgericht).

In dit proefschrift zijn twee opkomende technologieën ex-ante beoordeeld: nanotechnologie en witte biotechnologie. Deze beide technologieën worden van zeer groot belang geacht in de chemische industrie en materiaaltechnologie met grote mogelijkheden voor de toekomst (van beide technologieën wordt wel gezegd dat ze een revolutie teweeg zullen brengen in de wetenschap en maatschappij). Het type technologie beoordeling dat is toegepast wordt ‘life cycle engineering (LCE)’ genoemd (vrij vertaald als ‘levenscyclus techniek’). Life cycle engineering omvat de integratie van ‘levenscyclus analyse (LCA)’ en ‘life cycle costing (LCC, vrij vertaald als ‘levenscyclus kostenanalyse’). LCA is een methode om de milieubelasting van een product of technologie over zijn gehele levenscyclus te bepalen (van ‘wieg’, d.w.z. grondstoffen gebruik, tot ‘graf’, d.w.z. de afval fase). LCC is een soortgelijke methode maar richt zich

op economische aspecten. Life cycle engineering heeft als doel om de prestatie van een product te verbeteren over zijn gehele levenscyclus.

Op dit moment staat het concept 'life cycle engineering' nog in de kinderschoenen en is daarom niet altijd toereikend om technologieën op alle relevante aspecten te beoordelen. Met name voor ex-ante beoordelingen die zich richten op toekomstige technologieën of technologieën die nog in ontwikkeling zijn biedt het 'life cycle engineering' concept niet altijd genoeg bruikbare middelen. Het onderzoek in dit proefschrift heeft daarom allereerst tot doel bij te dragen aan de volgende onderzoeksvraag:

Op wat voor manier kan het bestaande life cycle engineering concept worden verbeterd of uitgebreid ten einde een completere ex-ante beoordeling van nieuwe technologieën mogelijk te maken en welke problemen of onzekerheden dienen nog te worden opgelost?

Voor witte biotechnologie is het erg belangrijk dat gezondheidsrisico's voor de mens in een vroeg stadium worden geïdentificeerd. Op dit moment zijn bestaande methoden hiervoor ontoereikend. Dit proefschrift heeft daarom tot doel bij te dragen aan de ontwikkeling van zo'n methode met het beantwoorden van de volgende deelvraag:

Op wat voor manier kan een algemene ex-ante beoordeling van conventionele risico's worden uitgevoerd voor chemicaliën met inachtneming van de gehele levenscyclus (d.w.z. van wieg tot fabriekspoort plus afvalfase)?

Op het niveau van de inventory gegevens (dat zijn de materiaal, energie en transport benodigdheden plus de emissies naar bodem, water en lucht) zijn ook verbeteringen van de LCE methodiek mogelijk: het vergelijken van een nieuw product dat slechts nog in het laboratorium wordt geproduceerd met een bestaand product blijkt soms lastig, omdat levenscyclus gegevens voor toekomstige grootschalige productie van het nieuwe product vaak niet beschikbaar zijn (zoals bijvoorbeeld voor nanokomposieten of polymeren zonnecellen).

In dit proefschrift wordt getracht een bijdrage te leveren aan deze kwestie. De volgende deelvraag is geformuleerd:

Hoe kunnen inventory gegevens worden afgeschat die representatief zijn voor de grootschalige industriële praktijk van producten of technologieën die nog in de laboratorium fase verkeren?

Naast deze methodologische kwesties richt het onderzoek in dit proefschrift zich op de ex-ante analyse van nanotechnologie en witte biotechnologie. Gezien het belang van deze

twee opkomende technologieën is er een vraag naar de analyse van kansen en risico's in een vroeg stadium. Volledige analyses naar alle aspecten van deze technologieën is niet mogelijk in slechts een enkel proefschrift, maar de ex-ante analyse van deelgebieden van deze technologieën is wel mogelijk. In dit proefschrift worden de volgende deelvragen beantwoord:

Wat zijn de kansen en risico's van nanotechnologie vanuit een milieu- en economisch oogpunt, waarbij de analyse zich richt op polymeren nanokomposieten en polymeren zonnecellen?

Wat zijn de kansen en risico's van witte biotechnologie, waarbij gekeken wordt naar gezondheidsrisico's voor de mens en waarbij de analyse zich richt op de biologische productie van polytrimethyleen terephthalaat (PTT), polyhydroxyalkanoaten (PHA) en ethanol?

De hierboven geformuleerde onderzoeksvragen worden beantwoord in de hoofdstukken 2-6.

Hoofdstuk 2 beschrijft een studie naar het gebruik van een polypropyleen (PP)/ klei nanokomposiet als inpakfolie, broeikasfolie en als autopaneel. Het doel van de studie is om milieu-impacts en kosten te evalueren gedurende de gehele levenscyclus van de producten vervaardigd uit de polypropylenen nanokomposiet. De referentie materialen zijn: puur polypropyleen voor de inpakfolie, puur polyethyleen voor de broeikasfolie en glasvezelversterkt polypropyleen voor de autopanelen. In alle drie de gevallen resulteerde het gebruik van de polypropylenen nanokomposiet in een reductie van het materiaalgebruik voor dezelfde functie in vergelijking met de conventionele (referentie) materialen. Het lijkt misschien vanzelfsprekend dat de milieubelasting van een product afneemt wanneer minder materiaal gebruikt wordt. De productie en toevoeging van nanodeeltjes aan een polymeer kan echter voor extra milieubelasting zorgen. Er bleken echter duidelijke milieuvoordelen over de gehele levenscyclus in het geval de polypropylenen nanokomposiet gebruikt wordt voor broeikasfolie. Er zijn enkele kostenvoordelen in het geval de nanokomposiet gebruikt wordt voor de productie van broeikasfolie en autopanelen. Als de prijs van nanoklei lager is dan € 5000,- per ton dan zijn er ook kostenvoordelen voor het gebruik van de nanokomposiet voor inpakfolie.

In hoofdstuk 2 wordt het gebruik van de Ashby materiaal indexen geïntroduceerd voor het afschatten van de hoeveelheid nieuw materiaal in vergelijking met een bestaand materiaal voor een zelfde functie. De Ashby indexen blijken een bruikbaar middel voor ex-ante analyses van materiaalbehoefte voor nieuwe materialen. Hoewel het een globale methode is, biedt het toch een eerste schatting van de invloed van materiaal

eigenschappen (zoals de Young's modulus, treksterkte en dichtheid) op de materiaalbehoefte en als zodanig kan het gebruikt worden als gegevens uit de praktijk niet voorhanden zijn.

In hoofdstuk 3 worden mogelijke voordelen onderzocht van het versterken van polymeren met nanodeeltjes voor structurele toepassingen door te kijken naar zowel mechanische eigenschappen als milieubelasting. Voor het bepalen van de mechanische eigenschappen worden de Ashby materiaal indexen voor stijfheid en sterkte gebruikt. Voor de berekening van de milieubelasting wordt de levenscyclus analyse (LCA) methode toegepast waarbij gekeken wordt naar niet-hernieuwbaar energiegebruik. Het is gebleken dat niet-hernieuwbaar energiegebruik een goede maat is voor ook andere milieupacts. Het niet-hernieuwbaar energiegebruik wordt vervolgens gedeeld door de geschikte Ashby index voor de berekening van het 'functie-gerelateerde niet-hernieuwbaar energiegebruik'. Drieëntwintig nanokomposieten zijn onderzocht, gebaseerd op een polymeren matrix bestaande uit een thermoplast of een thermoset en lipofiel montmorilloniet, silica, koolstof nanobuizen (enkel en dubbelwandig) of calcium karbonaat als vulmiddel. Zeventien van deze nanokomposieten lieten een afname zien van het functie-gerelateerde energiegebruik met toenemende vulmiddel concentratie. Hieruit wordt de conclusie getrokken dat het gebruik van nanodeeltjes als vulmiddel voordelen kan hebben zowel vanuit milieuoogpunt als met betrekking tot de mechanische eigenschappen.

Wanneer nanotechnologie succesvol blijkt voor grootschalige toepassingen is het zeer waarschijnlijk dat grote hoeveelheden nanokomposieten in afvalverbrandingsinstallaties (AVI) terecht komen. Verschillende studies hebben aangetoond dat nanodeeltjes schadelijk kunnen zijn voor de gezondheid en voor het milieu. Op dit moment is er geen eenduidig bewijs dat alle nanodeeltjes veilig worden verwijderd uit de rookgassen die vrijkomen bij de verbranding van nanokomposieten in AVI's. In hoofdstuk 4 wordt een voorstudie gedaan naar wat er met nanodeeltjes gebeurt tijdens de afvalverbranding en wat het vermogen is van AVI's om ze uit de rookgassen te verwijderen.

Het blijkt dat er vele primaire en secundaire nanodeeltjes vrijkomen bij de verbranding van nanokomposieten en deeltjes die kleiner zijn dan 100 nanometer blijken onvoldoende te worden verwijderd. Van de nanodeeltjes die onderzocht zijn in dit proefschrift blijken er risico's te zijn voor aluminium oxide, calcium karbonaat, magnesium hydroxide, POSS, silica, titanium oxide, zink oxide, zirconia, mica, montmorilloniet, talk, kobalt, goud, zilver, carbon black en fullerenen.

Gezien het feit dat deze analyse gebaseerd is op een literatuur-/computer studie zonder daadwerkelijke experimenten wordt vervolgd onderzoek aanbevolen om helder te krijgen

welke nanodeeltjes daadwerkelijk worden uitgestoten naar het milieu en wat hun gezondheidseffecten zijn.

Het gebruik van polymeren voor zonnepanelen wordt geacht verscheidene voordelen te hebben boven de huidige kristallijn silicium technologie. Verwachte voordelen zijn dat de materialen makkelijker te verwerken zijn en dat de technologie goedkoper is. Hoofdstuk 5 bevat een milieu- en economische analyse van polymeren dunnefilm zonnepanelen op een glas ondergrond en zonnepanelen met een flexibele ondergrond en de resultaten worden vergeleken met literatuurgegevens van multikristallijn silicium- en andere typen zonnepanelen.

Omdat de levensduur van polymeren zonnecellen momenteel nog veel lager is dan van silicium zonnecellen, worden de zonnepanelen eerst per watt-peak vergeleken en wordt vervolgens de minimale levensduur berekend die een polymeren zonnecel moet hebben om een vergelijkbaar milieuimpact te hebben als een silicium zonnecel. Uit de analyse blijkt dat per watt-peak vermogen, de milieuimpacts in vergelijking met het multikristallijn silicium zonnepaneel 20-60% lager zijn voor het polymeren zonnepaneel paneel op de glas ondergrond en 80-95% lager voor het polymeren paneel met een flexibele ondergrond. Ook in vergelijking met dunnefilm CuInSe en dunnefilm silicium blijken de impacts van de polymeren panelen, per watt-peak, lager. De minimale levensduur om gelijke milieuimpacts te hebben als multikristallijn silicium zonnepanelen is ruwweg 10-20 jaar voor polymeren zonnepanelen op glas en 1-5 jaar voor flexibele polymeren zonnepanelen.

De kosten per watt-peak van polymeren zonnepanelen op glas zijn ongeveer 20% hoger in vergelijking met multikristallijn silicium zonnepanelen. Het kan echter zijn dat dit een overschatting is, gezien de onzekerheden. Voor de flexibele zonnepanelen zijn geen kostengegevens beschikbaar. In het geval de efficiëntie en de levensduur van polymeren zonnepanelen toeneemt, kunnen zowel panelen op glas als de flexibele panelen een milieuvriendelijk en goedkoop alternatief worden voor multikristallijn silicium zonnepanelen.

Hoofdstuk 6 beschrijft de totstandkoming en toepassing van een generische aanpak voor de vergelijkende analyse van risico's met betrekking tot de productie van chemicaliën met witte biotechnologie versus petrochemische processen. Witte biotechnologie wordt gekenmerkt door het feit dat biologische grondstoffen worden gebruikt in tegenstelling tot de fossiele grondstoffen die gebruikt worden in de petrochemie. Het doel van deze studie was te onderzoeken of de productie van chemicaliën met witte biotechnologie minder conventionele risico's met zich meebrengt dan de productie met petrochemische processen. Conventionele risico's zijn risico's van algemeen aanvaarde processen, zoals fabricage, afvalverbranding en transport en niet de risico's van genetisch gemodificeerde

micro-organismen en planten. De aanpak in dit proefschrift combineert klassieke methoden van risicoanalyse (voor een groot gedeelte gebaseerd op toxicologie), zoals ontwikkeld door de levenscyclus analyse (LCA) gemeenschap, met statistieken van industriële rampen, ongelukken en werkgerelateerde ziekten. Daarbij dekt het de gehele procesketen voor zowel biologische als petrochemische producten van wieg-tot-graf.

De methode is toegepast op vijf producten: Op de plastics polytrimethyleen terephthalaat (PTT), polyhydroxyalkanoaat (PHA), polyethyleen terephthalaat (PET) en polyethyleen (PE) en op ethanol. In het geval van PTT en ethanol is biologische productie vergeleken met petrochemische productie. PHA, een biologisch product, is vergeleken met PET en PE, beiden petrochemische producten.

De resultaten laten zien dat de conventionele risico's van de producten geproduceerd met witte biotechnologie lager zijn dan die van de petrochemische producten. Echter, als de onzekerheden worden meegenomen met betrekking tot de grote spreiding van de input data, de (onvolledige) dekking van emissies door de Environmental Priority Strategies (EPS) 2000 methode en de onzekerheden van de aannamen gemaakt in deze studie (namelijk groot tot zeer groot), dan valt het verschil in de resultaten tussen de biologische en de petrochemische producten zeker binnen de onzekerheidsmarge. Om die reden is meer onderzoek nodig om de onzekerheden te verkleinen voordat geconcludeerd kan worden dat de conventionele risico's van producten geproduceerd met witte biotechnologie lager zijn dan die van producten geproduceerd uit fossiele grondstoffen.

In dit proefschrift zijn de kansen en risico's van nanotechnologie en witte biotechnologie ex-ante bestudeerd. Daarnaast heeft dit proefschrift bijgedragen aan een verbetering en uitbreiding van de bestaande methodologie op het gebied van life cycle engineering, wat een vollediger ex-ante beoordeling van nanotechnologie en witte biotechnologie mogelijk maakt. Uit de studie kunnen de volgende conclusies getrokken worden met betrekking tot deze methodische vraagstukken:

- Voor nieuwe technologieën die nog niet op de markt zijn, dienen procesgegevens uit het laboratorium geëxtrapoleerd te worden naar een realistische schatting voor de industriële praktijk. Voor de case studies uit dit proefschrift was dit mogelijk door inventory gegevens uit het laboratorium te gebruiken voor materiaal- en energiegebruik en gegevens over gebruikte processen (zoals extrusie, sproeidrogen, chemisch opdammen etc.) en deze te combineren met gegevens uit de grootschalige industriële praktijk. Wanneer een realistische set materiaal en energiegegevens is bepaald die representatief is voor de industriële praktijk, kan een analyse worden gemaakt van de milieupacts.
- Wanneer twee materialen (een nieuw en een conventioneel) worden gebruikt voor een structurele toepassing, zal de materiaalbehoefte verschillen in het voordeel van het materiaal met de beste mechanische eigenschappen. Er is gebleken dat de

materiaal indexen van Ashby voor stijfheid en sterkte een vereenvoudigd, maar bruikbaar middel zijn voor het bepalen van de materiaalbehoefte van een nieuw materiaal in vergelijking met een conventioneel materiaal (voor toepassingen die worden bepaald door de mechanische eigenschappen).

- In hoofdstuk 6 is een nieuwe methode ontwikkeld voor het uitvoeren van een impact analyse, namelijk een uitbreiding voor de analyse van humane gezondheidsrisico's over de gehele levenscyclus van producten. Alle risico's worden uitgedrukt in 'verloren levensjaren'. De methode is met succes toegepast op de levenscycli van PTT, PHA, PET, PE en ethanol, maar kan ook worden toegepast op andere chemische producten.

Op het gebied van nanotechnologie zijn er goede kansen voor polymeren nanokomposieten en polymeren zonnepanelen. Voor het merendeel van de onderzochte nanokomposieten bleek dat de toevoeging van nanodeeltjes als vulmiddel de mechanische eigenschappen zodanig verhoogt dat mogelijke extra impacts als gevolg van de productie en inmenging van nanodeeltjes gecompenseerd worden (gezondheidsrisico's zijn hier niet meegenomen). Er kan geconcludeerd worden dat het gebruik van nanodeeltjes voor de versterking van nanokomposieten voordelen heeft vanuit milieuoogpunt. Afhankelijk van de prijs van nanoklei kunnen er ook economische voordelen zijn. Risico's zijn voornamelijk de toxiciteit van de nanodeeltjes en de kans dat ze worden uitgestoten naar het milieu bij de afval verbranding van nanokomposieten.

Polymeren zonnepanelen zouden kunnen concurreren met bestaande zonnecel technologieën, maar voorwaarde is wel dat de levensduur drastisch omhoog gaat. De belangrijkste uitdagingen op het gebied van polymeren zonnecel technologie zijn dan ook het verhogen van de levensduur enerzijds en het verhogen van de efficiëntie voor de omzetting van licht in elektriciteit anderzijds.

Voor witte biotechnologie zijn geen verontrustende risico's gevonden. Uit de studies kwam naar voren dat de risico's van alle biologisch geproduceerde producten lager zijn dan die van de petrochemische producten. Echter, de onzekerheden zijn aanzienlijk en daarom is meer onderzoek nodig om dit met meer zekerheid te kunnen stellen, ook al lijken de resultaten nu in het voordeel van de biologische producten.

In dit proefschrift zijn met succes ex-ante analyses toegepast op producten geproduceerd met nanotechnologie en witte biotechnologie. De bestaande methodologie is verbeterd en uitgebreid. De Ashby methode bleek een bruikbaar middel voor het schatten van de materiaal behoefte van nieuwe materialen. Daarnaast is aangetoond hoe gegevens voor de industriële praktijk geschat kunnen worden op basis van laboratorium gegevens. Deze bijdragen vormen echter een eerste aanzet en bieden nog ruimte voor verbetering van de gehanteerde aanpak. Op basis van de analyses in dit proefschrift blijken er goede kansen

te zijn voor nanotechnologie en witte biotechnologie. Echter, om deze conclusies meer kracht bij te kunnen zetten en om de methoden voor ex-ante analyses verder te verbeteren bevelen wij vervolgonderzoek aan. Met name de vertaling van laboratorium gegevens naar een betrouwbare schatting van de industriële praktijk zou uitgebreider onderzocht moeten worden. Daarnaast dienen experimenten gedaan te worden om het precieze lot van nanodeeltjes in een afvalverbrandingsproces helder te krijgen.

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Lex

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About the author



Lex Roes was born in Amsterdam on April 13th 1976, but grew up in the south of the Netherlands. After graduating from grammar school he studied medical biology and environmental biology at the University of Amsterdam but later went over to environmental science at Utrecht University. He got his master degree in 2004. Lex did his master thesis at the department of Science, Technology and Society where he gained his first experience with ex-ante life cycle engineering; He made an environmental and economic assessment of the bio-based production of succinic acid and acetic acid. After graduation, he was offered a PhD position at the same department. He performed several studies involving life cycle assessment (in the context of this thesis but also for ROOTS Biopack – he studied a bagasse tray- and for DSM – he studied several routes for the production of bio-based succinic acid). Furthermore he performed several studies on monitoring energy efficiency developments in the Dutch industry in cooperation with Energieonderzoek Centrum Nederland (ECN) and contributed to a project on global energy efficiency achievements at Ecofys.

From August-December 2010 Lex did a research project at TNO Science and Industry (Eindhoven - the Netherlands) on sustainable design of industrial equipment.

Lex lives together in Den Bosch with Jowien de Groot.