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Ex-ante Life Cycle Assessment of polymer nanocomposites using organo-modified Layered Double Hydroxides for potential application in agricultural films

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ABSTRACT

Biodegradable agricultural films made from poly(butylene adipate-co-terephthalate) (PBAT) are an interesting alternative for the most commonly used low-density polyethylene (LDPE) films. Photodegradation of both types of polymers can be prevented by the addition of UV stabilizers. To prevent leaching of the additives from the films, the stabilizers can be intercalated in layered double hydroxides (LDH). When LDHs are exfoliated in the polymer a nanocomposite is formed with improved material properties.

An ex-ante cradle-to-grave life cycle assessment (LCA) is conducted on the application of nanoclays in agricultural mulching films. The PBAT/LDH nanocomposite is compared with PBAT and LDPE, which had both been UV-stabilized with the conventionally used compound Irganox 1010. Being key ingredients of the nanocomposites we prepare an ex-ante cradle-to-factory gate LCA for different nanoclay compositions, containing surfactants and the non-toxic UV stabilizer *p*-hydroxycinnamic acid, intercalated in LDH sheets.

Among the nanoclays, the lowest environmental impact is achieved by LDHs based on magnesium oxide/hydroxide and aluminum oxide/hydroxide, with the surfactant stearate as intercalated anion. Our comparative analysis of mulching films shows that the lowest non-renewable energy use and greenhouse gas emissions are obtained by LDPE films, which are recycled and incinerated with energy recovery after the second life cycle. However, recycling and energy recovery are not always applied, which makes the biodegradable PBAT an interesting alternative. Further study into the UV stability, tensile strength and bio-based feedstock for PBAT can indicate that PBAT containing LDH and *p*-hydroxycinnamic acid can be an environmentally friendly alternative for LDPE agricultural films containing the UV stabilizer Irganox 1010.

Introduction

In 2011, around 1.3 million tonnes of plastics, mostly fabricated from low-density polyethylene (LDPE), were used world-wide in the agricultural sector, *e.g.* for greenhouses, as mulching films and for small tunnels and temporary coverings of fruit trees. The agricultural sector benefits from this use by increased yields, earlier harvests, less reliance on herbicides and pesticides, better protection of food products and more efficient water use.[1,2] Although the end-of-life management of plastics has been improved and there is a growing public awareness of the consequences of plastic waste, only 46% of the agricultural plastic waste is recycled or recovered.[2] Interestingly, there is currently no binding regulation for agricultural plastic waste.[3] In several regions within Europe and in many other countries the waste is left on the field or burnt in an uncontrollable way.[1,4] Disposal in the field and landfilling lead to degradation of the quality of the soil and landscape, and threaten domestic and wild animals. Also the safety and quality of the food that is produced in the same field can be compromised. When the plastic waste is burnt, (environmentally) harmful substances are released to water, soil and air.[1] A solution to this plastic waste problem can be the use of biodegradable plastics which would prevent accumulation of plastics in the environment. Here, poly(butylene adipate-co-terephthalate) (PBAT) is an interesting option. PBAT is a petroleum-based compostable biodegradable plastic that can be processed with the same equipment as polyethylene and can replace LDPE in many applications, among which agricultural mulching films.[5] Moreover, it has the potential to be made from bio-based feedstock.[6]

When polymers are exposed to sunlight, UV-A and UV-B radiation can cause photodegradation of the polymers.[7] As a result, after a short time outdoors, plastic can undergo changes of color, surface cracking, embrittlement, reduction of gloss, chalking or gel formation (cross-linking).[8] The UV degradation can be reduced or prevented by inserting UV stabilizers in the polymer. Drawbacks of the addition of UV stabilizers are the presence of a concentration gradient, leaching out of the UV additives with a corresponding negative environmental impact and an impaired polymer structure by the increased photoreactivity.[7] Diffusion can be prevented by inserting the organic UV stabilizers into an inorganic host container acting subsequently as a filler, and forming a structure consisting of alternating layers of organic and inorganic materials, *i.e.* a layered double hydroxide (LDH).[7] LDH anionic clays have a material structure described by the formula $[\mathrm{M}^{\mathrm{II}}_{1\ x}\mathrm{M}^{\mathrm{III}}_{x}(\mathrm{OH})_2]^{x+}[A^{n-}_{\frac{x}{n}}\cdot m\mathrm{H_2O}]$. In this formula $\mathrm{M^{II}}$ and $\mathrm{M^{III}}$ represent metallic cations, mostly with double and triple positive charge ($\mathrm{Mg^{2+}}$, $\mathrm{Zn^{2+}}$, $\mathrm{Al^{3+}}$), respectively, and A^{n-} represents the interlayer anion. For the anions a wide range of anionic organic moieties can be used, for example UV stabilizers. The 2D-confinement of the organic UV stabilizer by the inorganic platelets prevents the UV stabilizer from migrating.[7] The LDH structure is represented in Figure 1. LDH platelet systems compare well with other naturally occurring clays, such as the smectite–type family, in terms of the platelet thickness and the ion exchange capacity.[9,10] The LDH can be melt-intercalated inside a polymer matrix, which results in a nanocomposite (Figure 2). In a nanocomposite material, where one of the composites is at nanoscale size and the nanomaterial represents less than 5 weight-%, the composite material benefits from a synergy due to the high surface area, *i.e.* large interaction with polymer chains, and high aspect ratio, *i.e.* pronounced barrier effects.[11,12]

When biodegradable plastics are used for agricultural films, the (non-biodegradable) additives are left in the field. Many plastic additives are hazardous for human health and the environment.[13] It is therefore important to find additives that are biodegradable and have no negative environmental impacts. Some types of LDHs are biocompatible; they are considered in the food industry[14], in drug delivery for taste masking[15] and even as gene reservoirs[16]. In a study by Coelho et al.[7] several *trans*-cinnamic acids were investigated as UV stabilizers. These are natural products found in the biosphere (*e.g.* occurring in cinnamon[17]) and are therefore expected to be biodegradable and to have a negligible or low environmental impact. Coelho et al.[7] compared *trans*-cinnamic acids incorporated in a polymer matrix with the nanocomposite of *trans*-cinnamic acids within an LDH structure. Totally exfoliated LDH-polymer nanocomposites have enhanced thermostability and UV stability. Furthermore, film barrier properties are increased and the mechanical properties are enhanced.[7]

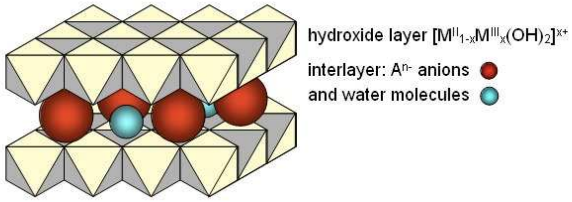


Figure 1 Structure of layered double hydroxide[18]

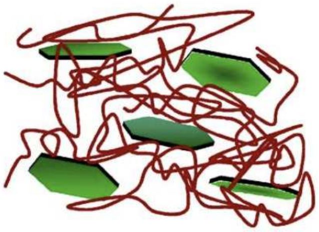


Figure 2 Exfoliated structure of LDH-polymer nanocomposites[19]

Before making investment decisions for large-scale production of LDH nanocomposites, it is important to assess the environmental impacts throughout the life cycle of the product, *i.e.* from cradle to grave - which comprises the production, use and disposal. With this knowledge it can be concluded whether the implementation of LDH in (bio)polymers is an improvement on the environmental performance of plastics compared to the conventional alternatives. The environmental performance is evaluated by an *ex-ante* Life Cycle Assessment (LCA). In an LCA all the natural resources used and the emissions released during the life cycle are inventoried in quantitative terms. The comparison of the environmental impacts among alternative product systems is enabled by studying a so-called functional unit, which represents the function of the product, rather than the amount of a product.[20] As is typical for most *ex-ante* LCA studies, the materials in this study are still in the R&D phase, which makes the assessment subject to substantial uncertainty.

Life Cycle Assessment

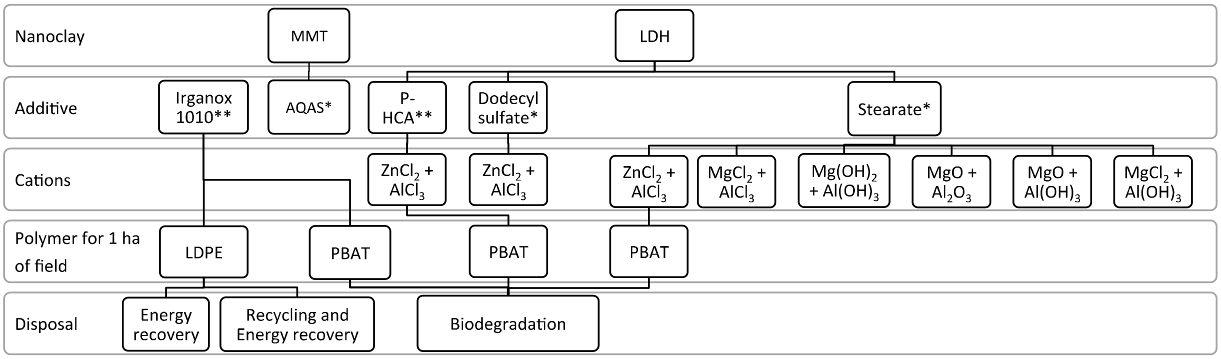
According to the ISO standard 14040:2006, an LCA consists of four phases: (1) goal and scope definition, where the functional unit and the system boundaries are defined, (2) inventory analysis, which comprises modelling of all activities including the inputs of resources to the system and emissions released by it, (3) impact assessment, where the data from the inventory analysis are converted into environmental impacts, and (4) interpretation, in which the results of the inventory analysis and the impact assessment are discussed, conclusions are drawn and recommendations are formulated.[20]

Goal and scope definition

The goal of this LCA is to assess and compare the environmental performance of several material compositions for agricultural mulching films. For this purpose, nanocomposites consisting of the biodegradable polymer PBAT mixed with nanoclay are compared with PBAT and with the conventional material LDPE which are both blended with the common UV stabilizer Irganox 1010. Among the nanoclays, layered double hydroxides (LDH) of several material compositions are compared with the cationic nanoclay montmorillonite (MMT). LDH is a novel nanomaterial while MMT has been used at commercial scale for several years.[12] We assess the cradle-to-factory gate impacts of combinations of nanoclays with different types of surfactants, which are added to enhance the dispersion in the polymers through a better organophilicity of the inorganic platelets, and the UV stabilizer *p*-hydroxycinnamic acid, which is sandwiched in the layered structure of the LDHs forming alternately *p*-hydroxycinnamic acid and inorganic platelets, i.e. a hybrid organic-inorganic material. The anionic surfactants stearate and dodecyl sulfate are used in the alternatives based on LDH, and the cationic surfactant alkyl quaternary ammonium salt is used in the case of MMT. The surfactants do not have UV stabilizing properties; this comparison is made to assess the environmental performance of several nanoclays before considering the addition of the UV stabilizer. The chemical compositions and XRD patterns of the LDHs based on zinc chloride and aluminum chloride are given in the Supporting Information. Literature data is used for the nanoclays based on magnesium.[21] Although the layered structure of the magnesium-based alternatives is comparable to the zinc-based nanoclays, the first material is less crystallized, leading to less structural information once dispersed into a polymer. The process to blend the nanoclays into the plastics for the mulching films is the same for the different nanoclay compositions, prompting us to continue with only two alternative LDH compositions to conduct a cradle-to-grave assessment for the use of nanocomposites as plastic agricultural mulching films with sufficient mechanical strength and high UV stability. The mulching film made of the PBAT nanocomposite of LDH nanoclay based on zinc and aluminum containing the UV absorber *p*-hydroxycinnamic acid is compared with PBAT and LDPE compounded with the conventional UV absorber Irganox 1010. The functional unit of the mulching film is defined as the coverage of 1 ha of land. To separately investigate the influence of LDH and *p*-hydroxycinnamic acid, the alternatives are also compared to a nanocomposite containing LDH with the surfactant stearate. However, this alternative has no UV stabilizing properties, in contrast with *p*-hydroxycinnamic acid and Irganox. An overview of the different alternatives is given in Figure 3.

The impact categories non-renewable energy use (NREU), climate change (greenhouse gas emissions), abiotic depletion, ozone layer depletion, photochemical oxidant formation, acidification, eutrophication, ecotoxicity and human toxicity are investigated for the system cradle-to-factory gate of the nanoclays (with additives). For the mulching films only the greenhouse gas (GHG) emissions and NREU are investigated, as impact data gaps exist for the other impact categories.

Figure 3 Overview of the alternatives studied for mulching film covering 1 ha of agricultural land. MMT = Montmorillonite, LDH = Layered double hydroxide, AQAS = alkyl quaternary ammonium salt, P-HCA = *p*-hydroxycinnamic acid. *Surfactants, **UV-stabilizers.



Inventory analysis

LDH nanocomposites are still in the R&D stage. Data are used from the laboratory and scaled up to the industrial level. The fabrication process of LDH is schematically represented in Figure 4. It is assumed that the reagents are converted with a yield of 100%. For the reaction a surplus of surfactants and UV stabilizers is added, which is recovered by reverse osmosis and reused (the energy use of the reverse osmosis unit is taken into account). The inventory data for the production of LDH are given in Table 1. Process data for the production of MMT were taken from the LCA study by Roes et al.[22] and are represented in Table 2. The Ecoinvent database (version 2.2) is chosen as source for background data for the life cycle inventory analysis. Materials that are not available in the database are represented by simplified process descriptions (see footnotes Table 1).

To cover 1 ha of agricultural land, 150 kg of low-density polyethylene (LDPE) are used (personal communication with Limagrain). When nanoclay is blended with polymers, the properties of the plastic improve. This makes it possible to use less material compared to the reference case (LDPE), while fulfilling the same function.[22] The weight reduction can be estimated by using Ashby's material indices.[23] Ashby defined material indices for different mechanical properties (*e.g.* stiffness or strength) of different categories of products (*e.g.* panel or beam). The indices are calculated based on data for material properties such as the Young modulus (E), tensile strength (σ_f) and density (ρ).[22,23]

Ashby's indices are inversely proportional to the amount of material needed, so the higher the index, the less material is needed for the same function. For the agricultural film it is assumed that the material design is strength-limited with the constraint 'Tie' (tearing is caused by a force parallel to the surface of the film).[22] This function is represented by the following formula, where M represents the mass, σ_f the tensile strength, and ρ the density:[24]

$$M = \sigma_f / \rho$$

The change of weight is estimated by the following formula:

$$\text{Change of weight (\%)} = \left(\frac{\sigma_f/\rho \ [\text{LDPE}]}{\sigma_f/\rho \ [\text{nanocomposite}]} - 1 \right) * 100$$

The values used in this formula are given in Table 3. LDPE used for agricultural films contains 1 weight-% of the UV stabilizer Irganox 1010 in order to ensure a minimum lifetime. These stabilizers are included in the weight of 150 kg.

The life cycle of LDPE nanocomposites is represented in Figure 5. LDPE is mixed with the UV stabilizers in the extrusion process. Two scenarios are investigated; one in which the LDPE is used once and afterwards incinerated with energy recovery, and another scenario where the plastic is recycled and after the second use phase incinerated. In the alternative in which plastic is recycled, the impact of two life cycles is calculated and the total impact is divided by two, to obtain the average impact per life cycle. The process for the fabrication of the polymer nanocomposite with LDH is the same as the process with MMT. In the case of plastics without nanomaterials, the processes *grafting, masterbatch* and *dilution* are omitted.

The material composition of PBAT is obtained from Brookes[25]. Processing data for PBAT are obtained from Berti et al.[26], as the synthesis they describe for poly(alkylene dicarboxylate)s is very comparable to the synthesis of PBAT. From this publication it appears that the esterification process is similar as for PET.[27] Feedstock data for PBAT are given in Table 4. After polymerization, the processing steps applied to make plastic films from PBAT are comparable to processing of LDPE (Figure 5). Normally, to improve the compatibility of the polymers with the nanoclay and improve the material properties, maleic anhydride, styrene and peroxides are added in a grafting process.[28] However, for mulching films the material requirements are not very high, as the plastic has to break when the plants grow larger. The grafting process is therefore omitted. In large extruders, mixing with the nanoclay can take place in the same process as product forming.[29] Therefore, in this study it is assumed that the dilution takes place in the extrusion phase.

Inventory data for incineration of LDPE is calculated based on the calorific value of the waste. The calorific value of mulching films decreases with increasing amounts of adhering soil.[30] With reference to the study by Briassoulis et al.[30] we assume a gross calorific value of 34.5 MJ/kg for LDPE mulching films with a thickness of 15 μm and contaminated by 42 wt% of soil. It is assumed that for every joule of heating value of the waste 0.12 joule of electricity and 0.12 joule of heat are recovered; this recovered energy avoids the production of electricity and heat from conventional resources.[22] The UV stabilizer is assumed to have the same heating value as the plastic.

In the recycling process the used LDPE films are shredded and washed twice. Then the flakes are dried and pellets are produced after two cycles of extrusion in order to remove impurities.[31] For the processes of hydrocycloning and filtration, which are also repeated once, the values reported by Roes et al.[22] are used. The calculations of centrifugation and the first extrusion cycle are based on the Promeco Extruder System® which dries the flakes and prepares them for traditional extruding.[32] Water is used in a closed cycle and therefore not included in the analysis.[33] The recycling efficiency is set to 86%[31] and the remaining waste is incinerated and replaced by virgin LDPE to obtain 150 kg of plastic. Loss of antioxidants during the use phase is compensated by the addition of new UV stabilizer for the re-use of recycled polymers.

In the case of PBAT, the polymer decomposes on the field. All the carbon content that is not released by photodegradation during the use phase is considered for biodegradation of PBAT. Incineration of PBAT is not considered, as one of the benefits of the biodegradability of PBAT is that the farmer does not have to collect the plastic waste. All the inventory data are represented in Table 5.

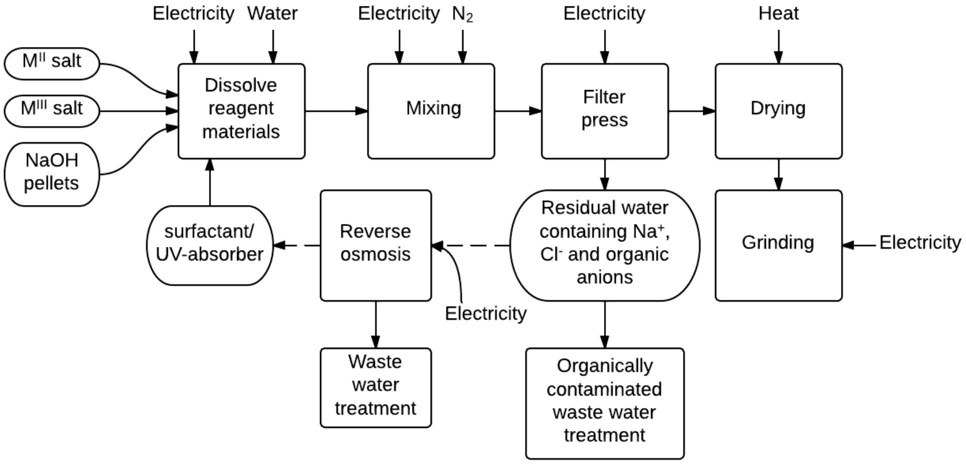


Figure 4 Production process of LDH

Table 1 Inventory data for the production of eight different LDH/surfactant/UV stabilizer combinations (1 kg each)

Input	Unit	ZnCl$_2$ + AlCl3 + Dodecyl sulfate	ZnCl$_2$ + AlCl3 + Stearate	ZnCl$_2$ + AlCl3 + P-HCA	MgCl$_2$ + AlCl3 + Stearate	MgCl$_2$ + Al(OH)3 + Stearate	Mg(OH)$_2$ + Al(OH)3 + Stearate	MgO + Al$_2$O3 + Stearate	MgO + Al(OH)3 + Stearate
ZnCl2[34]	kg	0.43	0.42	0.51					
MgCl2[35,36]	kg				0.33	0.33			
Mg(OH)2[36]	kg						0.20		
MgO[36]	kg							0.14	0.14
AlCl3 * 6 H2O[37]	kg	0.38	0.37	0.45	0.42				
Al(OH)3	kg					0.14	0.14		0.14
Al2O3	kg							0.09	
C12H25OSO3Na	kg	0.91							
C12H25OSO3Na	kg	-0.45*							

C18H35NaO2	kg		0.94		1.07	1.07	1.07	1.07	1.07
C18H35NaO2	kg		-0.47*		-0.54*	-0.54*	-0.54*	-0.54*	-0.54*
OH-C6H4-CH=CH-COOH	kg			0.62					
OH-C6H4-CH=CH-COOH	kg			-0.31*					
NaOH	kg	0.44	0.49	0.60	0.56	0.55			
Water	kg	7.22	7.47	8.02	7.82	7.74	5.00	5.00	5.00
N2	kg	4.04E-03	3.87E-03	3.48E-03	3.62E-03	3.68E-03	5.58E-03	5.58E-03	5.58E-03
Residual water	kg	7.22	7.47	8.02	7.82	7.74	5.00	5.00	5.00
Electricity									
Stirrer[38]	MJ	0.05	0.05	0.05	0.05	0.05	0.02	0.02	0.02
Pump and computer[39,40]	MJ	2.49E-03	2.50E-03	2.53E-03	2.52E-03	2.52E-03	2.39E-03	2.39E-03	2.39E-03
Filter press[22]	MJ	0.29	0.29	0.29	0.29	0.29	0.29	0.29	0.29
Reverse osmosis[38]	MJ	0.23	0.24	0.26	0.25	0.25	0.16	0.16	0.16
Grinding[22]	MJ	0.51	0.51	0.51	0.51	0.51	0.51	0.51	0.51
Heat									
Drying**	MJ	15.08	15.08	15.08	15.08	15.08	15.08	15.08	15.08
Heating**	MJ					2.18			

*Negative value indicates that the surplus is recovered and becomes available for reuse.

**Efficiency assumed of 50%. References represent sources for background data and calculations

Table 2 Material and energy input for 1 kg of MMT. Based on Roes et al.[22]

Input	Unit	Amount for 1 kg MMT
Bentonite	kg	0.65
Surfactant	kg	0.35
Fuel oil		
Spray drying	kg	0.10
Electricity		
Hydrocyclone	MJ	0.62
Spray drying	MJ	0.26
Organic modification	MJ	14.73
Filter press	MJ	0.07

Table 3 Material properties and estimated weight for functional unit

Alternative	Tensile strength (σ_f, MPa)	Density (ρ, t/m^3)	Estimated weight for functional unit (kg)
LDPE (1% Irganox 1010)	24[22]	0.923[22]	150
PBAT (1% Irganox 1010)	45*	1.26[41]	109
PBAT (5% LDH/*p*-hydroxycinnamic acid)	38*	1.26 (estimated)	129
PBAT (5% LDH/stearate)	49*	1.26 (estimated)	100

* The tensile strength values of PBAT are obtained from experiments in the laboratory frame. For the nanocomposite of PBAT with LDH/stearate, the tensile strength of the PBAT nanocomposite with 5% LDH/CO_3 is used; it is assumed that these materials have comparable properties.

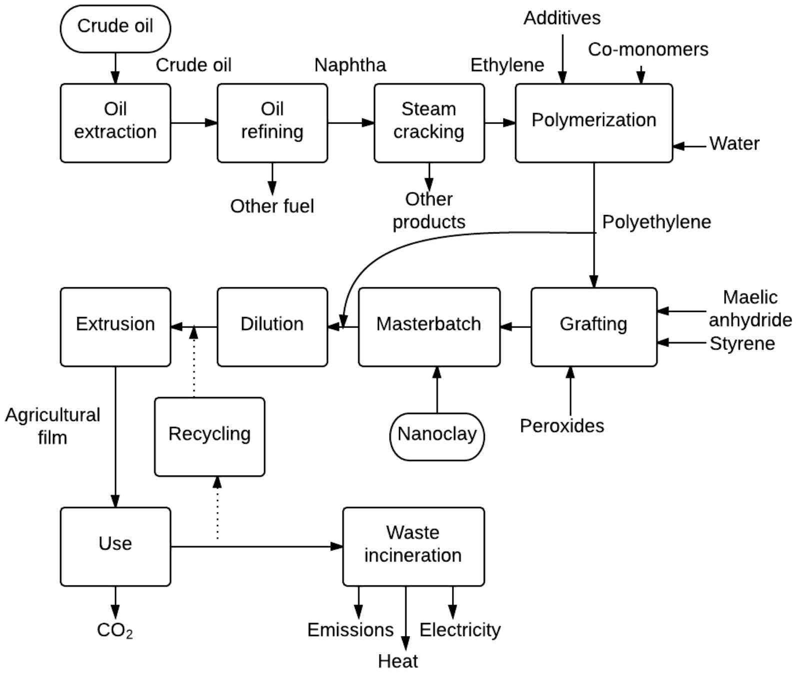


Figure 5 Life cycle of polyethylene nanocomposites. All processes require energy input, which is omitted for clarity. Based on Roes et al.[22]

Table 4 Feedstock requirements for 1 kg of PBAT

Input	Unit	Amount for 1 kg of PBAT
1,4-butanediol*	kg	0.41
Adipic acid*	kg	0.37
Terephthalic acid*	kg	0.33
Esterification[27]	MJ	7.60

*A synthesis efficiency of 90% is assumed. Based on Brookes[25]

Table 5 Inventory data for coverage of 1 ha of land with agricultural films

Inventory data	Unit	Amount for 1 ha of film
Cradle to factory gate - Energy and material input		
LDPE with 1% UV stabilizer		
LDPE	kg	148.5
UV stabilizer Irganox	kg	1.5
Electricity for extrusion	kg	150.0
PBAT with 1% UV stabilizer		
PBAT	kg	108.1
UV stabilizer Irganox	kg	1.1
Electricity for extrusion	kg	109.2
PBAT with 5% LDH - UV stabilizer		
PBAT	kg	122.9
LDH - *p*-hydroxycinnamic acid	kg	6.5
Electricity for masterbatch	MJ	19.6[22]
Electricity for extrusion	kg	129.3
PBAT with 5% LDH - surfactant		
PBAT	kg	95.3
LDH - stearate	kg	5.0
Electricity for masterbatch	MJ	15.2[22]
Electricity for extrusion	kg	100.3
Incineration of LDPE		
Incineration of LDPE	kg	150.0
Exported electricity	MJ	-1070.7*
Exported heat	MJ	-1070.7*
Recycling of LDPE		
Electricity for shredding	MJ	550.8[31]
Electricity for hydrocycloning	MJ	187.0[22]
Electricity for filtration	MJ	22.0[22]
Electricity for drying and extrusion	MJ	226.8[32]
Electricity for pelletising	MJ	345.62[31]
Incineration of waste (14%)	kg	21.4
Exported electricity	MJ	-115.5*
Exported heat	MJ	-115.5*
Virgin LDPE	kg	21.4
Extrusion (film)	kg	150.0
UV stabilizer Irganox	kg	1.5

Biodegradation of PBAT		
PBAT with 1% UV stabilizer	kg	108.1
PBAT with 5% LDH - UV stabilizer	kg	122.9
PBAT with 5% LDH - surfactant	kg	95.3

*Credits are given as energy recovery avoids the production of energy elsewhere. The recovered electricity substitutes the average market mix which is represented by the weighted average of 74.4% UCTE Electricity, 15.1% NORDEL Electricity, and 10.5% CENTREL Electricity (All medium voltage). The recovered heat replaces natural gas.[22]

Impact assessment

For the impact assessment the CML 2 baseline 2000 V2.05 method[42] is applied. The NREU is obtained with the method Cumulative Energy Demand V1.08.

The results of the impact assessment of the different nanoclay compositions with surfactants are represented in Figure 6 and Figure 7. Figure 6 shows that the material compositions containing magnesium and aluminum oxide/hydroxide score best on all impact categories, except terrestrial ecotoxicity and photochemical oxidation, where montmorillonite has the lowest impact. Considering the GHG emissions and NREU, which are often used to evaluate the environmental impact of a product, the preferred material would be LDH based on magnesium hydroxide/oxide and aluminum hydroxide/oxide, followed by montmorillonite. Comparing the surfactants dodecyl sulfate with stearate, stearate has a lower impact for most impact categories. Figure 7 shows the contribution of the production processes and reagents to the NREU. Data labels are added to indicate the largest contributors. The highest contribution is caused by the surfactants and drying of the clay. As montmorillonite is a natural product, the surfactants have to be added in a separate process, which has a significant environmental impact. The nanoclay containing *p*-hydroxycinnamic acid is not included in the same graph because the additives (*p*-hydroxycinnamic acid and the surfactants) do not provide the same function and are therefore not directly comparable. Also the values for the impact of *p*-hydroxycinnamic acid are in a higher order of magnitude, which would reduce the clarity of the figure.

Figure 8 shows how the NREU of *p*-hydroxycinnamic acid is built up, adding up to a total of 1564 MJ per kg. Due to lack of data on industrial production this calculation is based on literature data, assuming conversion efficiencies of 90%.[43–52] It is assumed that a Wittig reaction is used in the production process, which contributes largely to the environmental impact due to the use of triphenylphosphine.

The UV stabilizer Irganox 1010 is a hindered phenol, based on 2,6-di-tert-butylphenol. Different types of stabilizers are obtained by substituents in the 4-position of the phenol group.[53] The production process of Irganox 1010 was described by Tanimoto & Toshimitsu[54] and Fiege et al.[55]. Molar conversion efficiencies of 90% are assumed. The NREU build-up of Irganox 1010 is represented in Figure 9, with a total of 158 MJ/kg.

To calculate the environmental impacts related to the production of petrochemical PBAT, impact data for adipic acid are obtained from Cok et al.[56] and for terephthalic acid from a forthcoming publication of Tsiropoulos et al.[57]. For the polymerization of PBAT the life cycle impact assessment data for PET according to PlasticsEurope[27] are used. Impact data on biodegradation of PBAT is obtained from Hermann et al.[58]. The scenario 'home composting' of Hermann et al. is applied. The alternative scenario 'industrial composting' uses higher temperatures (50-60˚C) and the biomass is mixed more frequently while the plastics in the soil will only be ploughed. Only for the carbon credits for avoided soil conditioners the industrial composting scenario is applied, as this scenario is more representative for the agricultural sector where straw is used rather than peat. This is also the case for the value of NREU, as the difference between the two scenarios is caused by the replacement of peat. The fact that soil conditioners are avoided reduces the GHG emissions of biodegradation with 11%.

The results of the impact assessment of the agricultural films are given in Figure 10 and Figure 11. It appears that LDPE with conventional UV stabilizers has lower GHG emissions and NREU than petrochemical PBAT, both with conventional UV stabilizers and with LDH nanoclay. Regarding the NREU, this lower score is caused by the energy credits that are given in the incineration process. The PBAT films cause higher GHG emissions due to the impact of the production of petrochemical PBAT. Among these product systems, the best option seems to be LDPE with conventional UV stabilizers, which is recycled after the first use phase and after the second use phase incinerated with energy recovery. The impact of *p*-hydroxycinnamic acid is estimated to be very high, explaining the relatively high environmental impact of the product system containing this material. The impact of LDH nanoclay with the surfactant stearate is much lower. Due to the improved material properties less plastic can be used for the same function, and the alternative becomes comparable to PBAT without LDH (PBAT – Irganox).

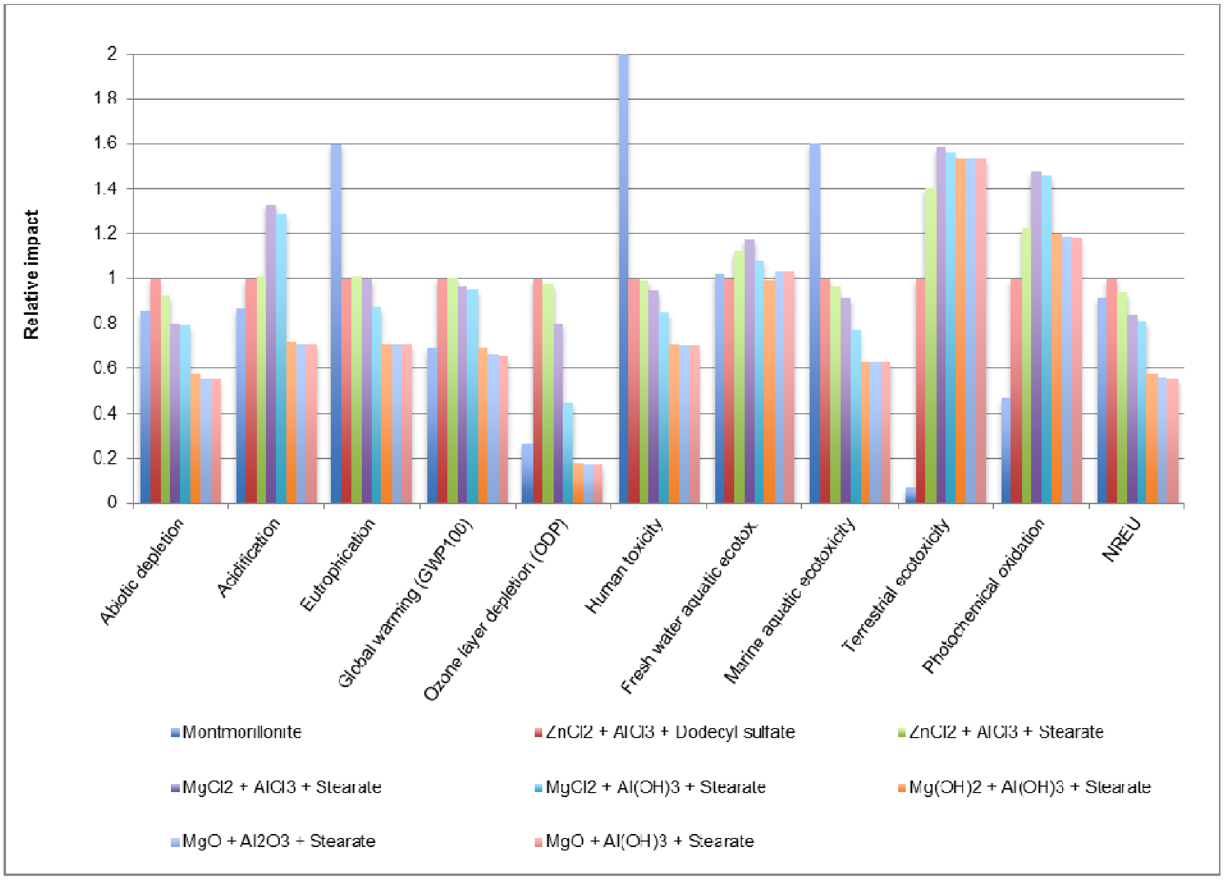


Figure 6 Relative results of the impact assessment of 1 kg of nanoclay with surfactants, including recycling of surfactants of the LDH. The values are shown relative to the alternative based on zinc chloride, aluminum chloride and dodecyl sulfate.

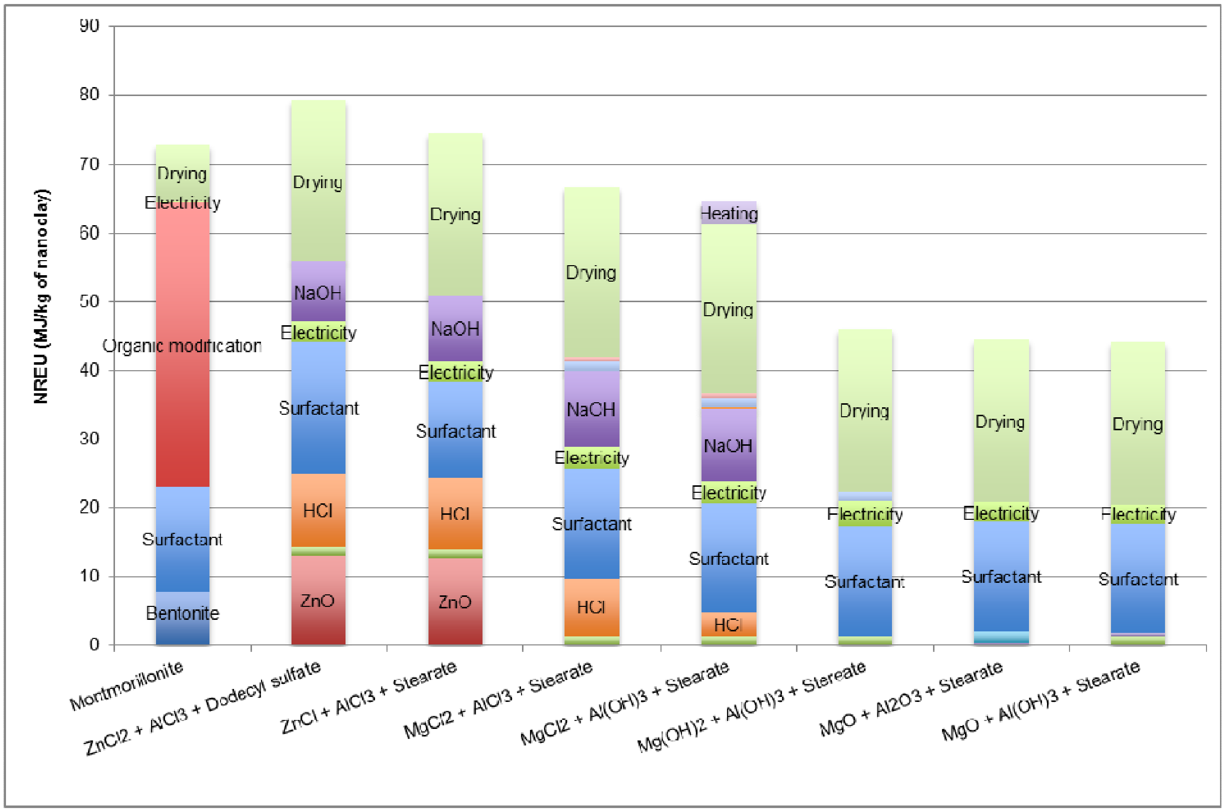


Figure 7 NREU (MJ) of one kg of nanoclay with surfactants (cradle-to-factory gate)

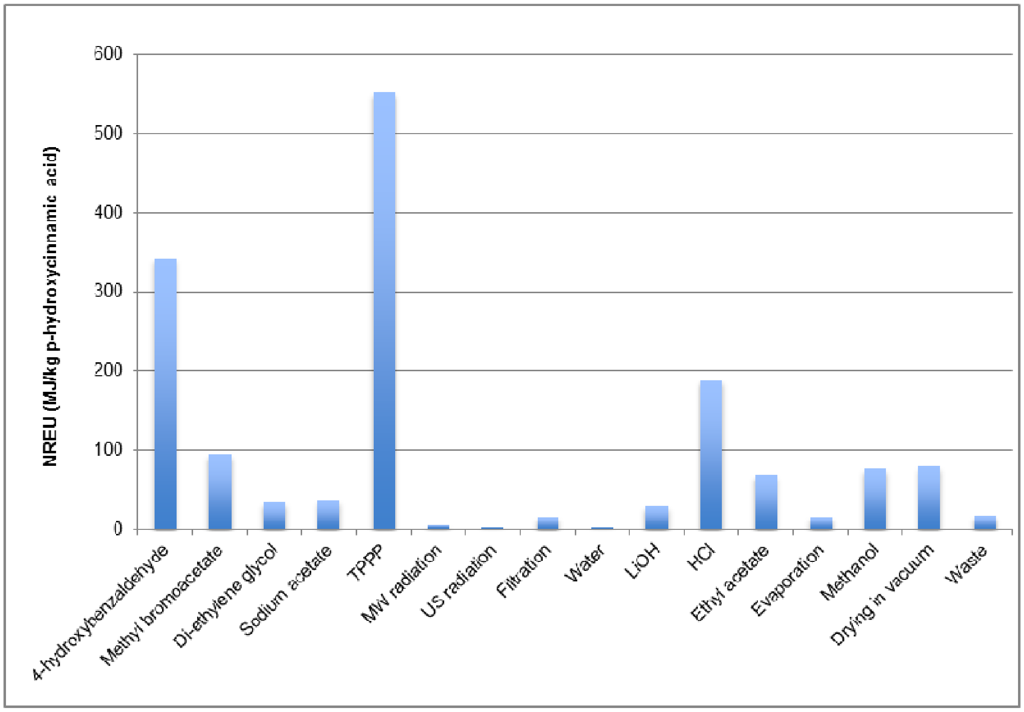


Figure 8 NREU of *p*-hydroxycinnamic acid (cradle-to-factory gate) (TPPP = triphenylphosphine)

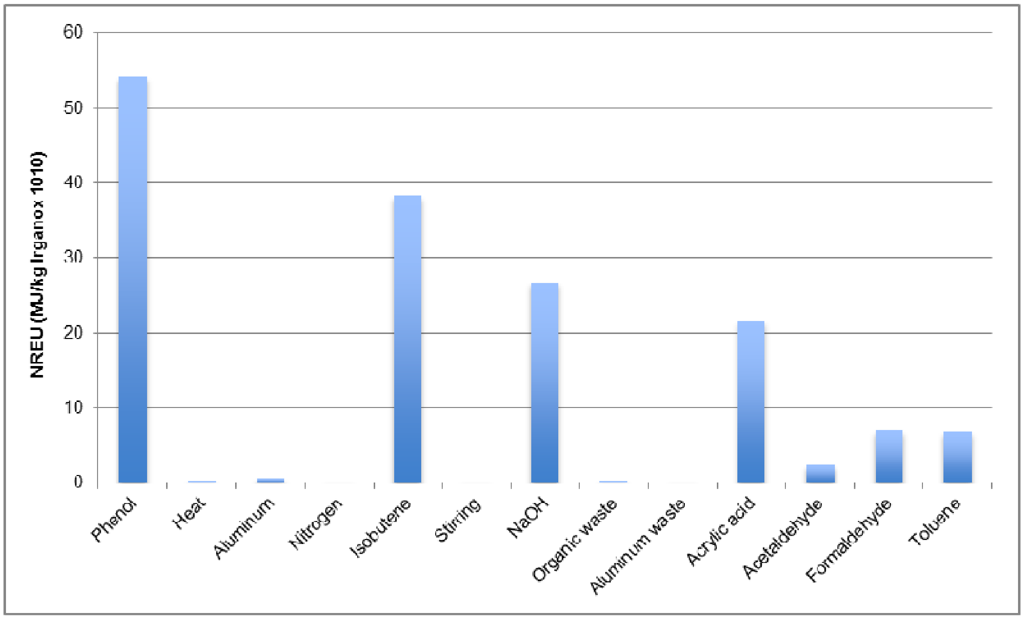


Figure 9 NREU of Irganox 1010 (cradle-to-factory gate)

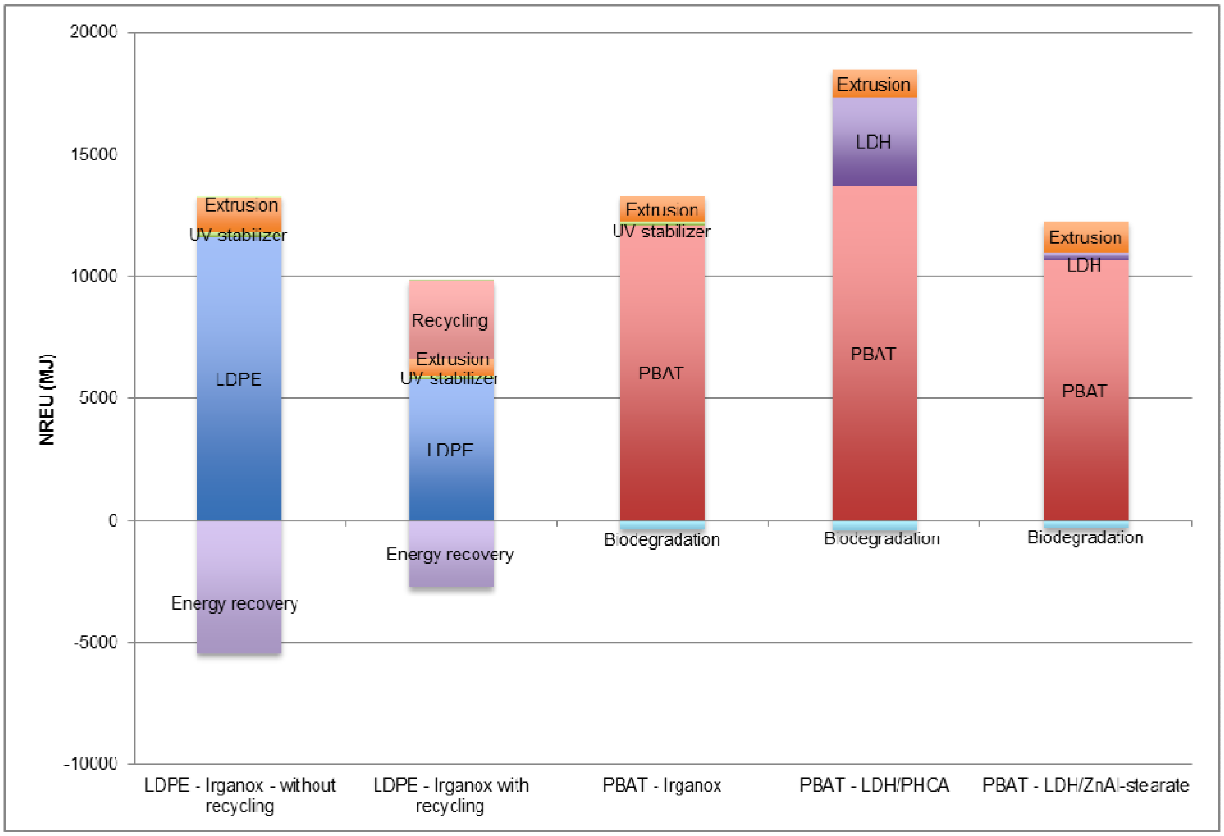


Figure 10 NREU for coverage of 1 ha of land with agricultural films (PHCA = p-hydroxycinnamic acid).

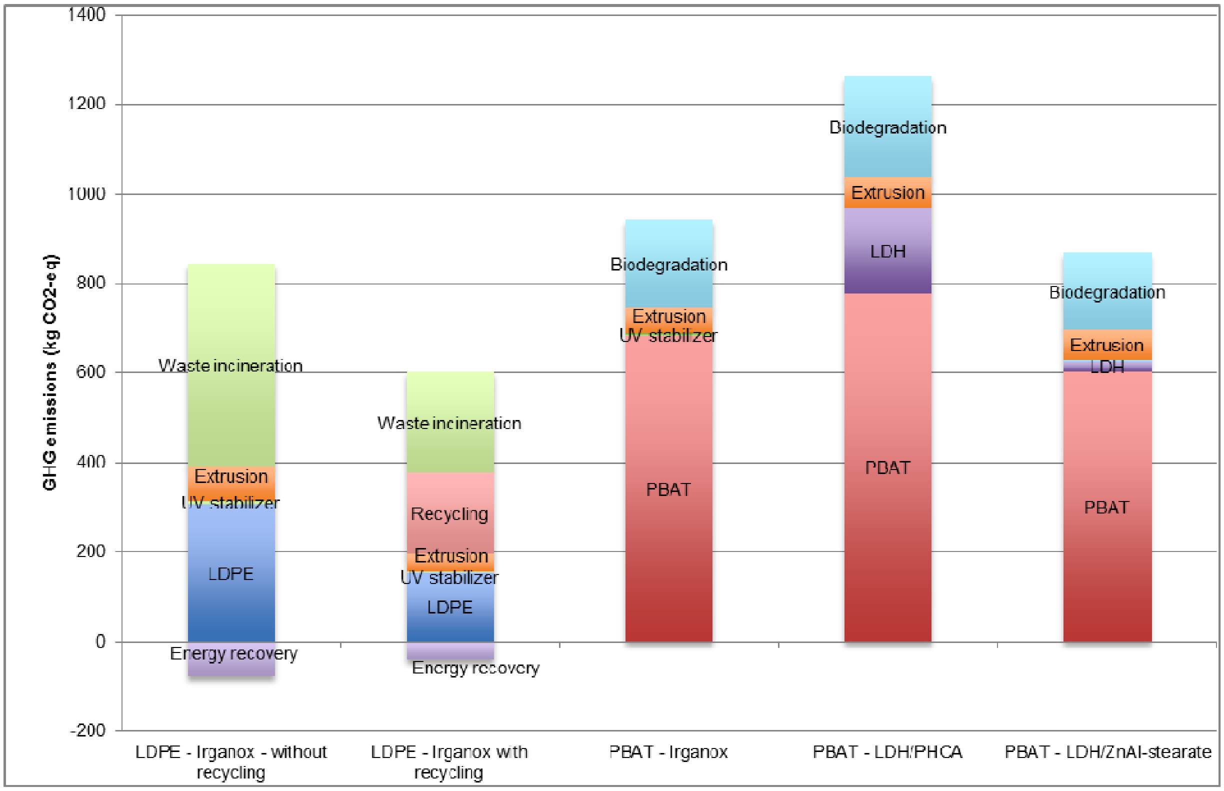


Figure 11 GHG emissions for coverage of 1 ha of land with agricultural films (PHCA = p-hydroxycinnamic acid)

Bio-based alternative to PBAT

It has so far been assumed that PBAT is produced from petroleum-based feedstocks. Research has been ongoing on bio-based alternatives for the reagents of PBAT. 1,4-butanediol could be fabricated by catalytic reduction of bio-based succinic acid. A bio-based alternative for terephthalic acid could be 2,5-furan dicarboxylic acid. This material is made by the oxidation of 5-hydroxymethylfurfural (HMF).[38] Several options are known to replace petroleum based adipic acid by renewable acid[38], among which succinic acid.[59]

However, many biomaterial technologies are still in the R&D phase although the economical perspectives are promising.[60,61] To replace PBAT by “PBSF” (as adipic acid is replaced by succinic acid and terephthalic acid by furan dicarboxylic acid, forming poly(butylene succinate-co-butylene furandicarboxylate)), the biodegradability and the material properties should be comparable which would remain to be proven.

To assess whether PBSF as bio-based alternative to petrochemical PBAT would be environmentally competitive with LDPE, the LCA is redone with inventory and impact values for PBSF. For these data a range is used based on optimistic and pessimistic values from Patel et al.[38], Reverdia[59] and Eerhart et al.[62]. While it is plausible to account for carbon storage when bio-based materials are used in long-lived durable applications,[63] no credits are given for the product systems based on PBSF because the CO_2 that was initially captured during the growth of the biomass is released after a relatively short period of time during degradation of the material. Figure 12 and Figure 13 show that agricultural films from PBSF could have lower NREU and GHG emissions than films made of petroleum-based LDPE. However, this is mainly the case when the estimates for the GHG emissions and NREU for the reagents of PBSF fall within the optimistic part of the range used in this study. It is however very probable that the GHG emissions of PBSF with Irganox 1010 and of PBSF-LDH/ZnAl-stearate will be lower than the emissions of LDPE (without recycling; see Figure 13).

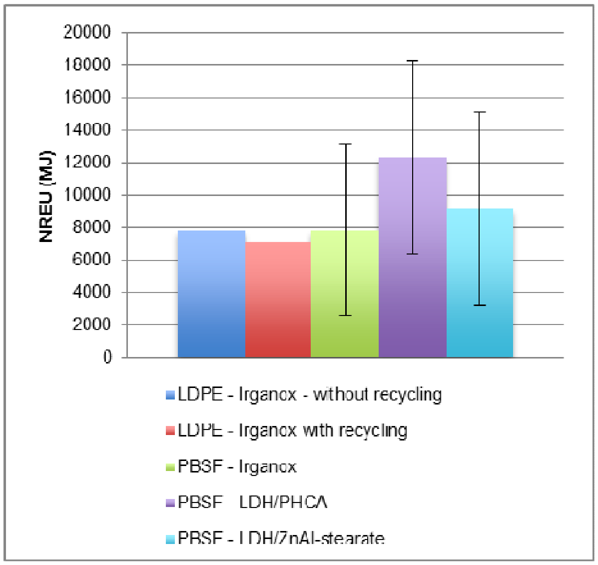


Figure 12 NREU for coverage of 1 ha of land with agricultural films, using PBSF

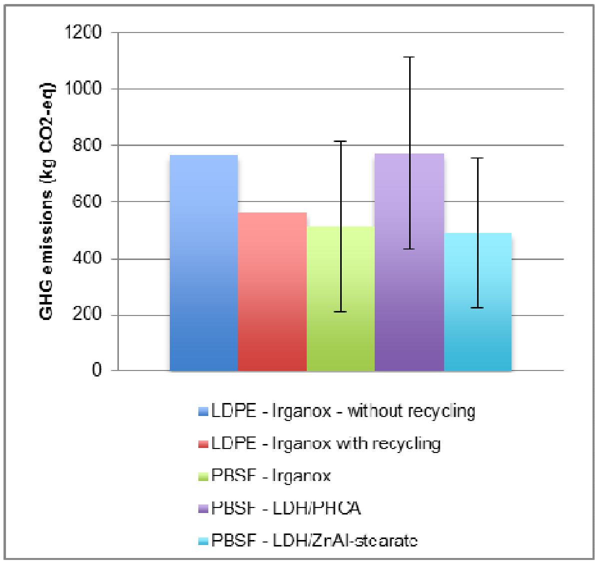


Figure 13 GHG emissions for coverage of 1 ha of land with agricultural films, using PBSF

Interpretation

Next to the fact that there is always some uncertainty present in the LCAs available in databases such as Ecoinvent, other sources of uncertainty are discussed here.

Inventory data

LDH is hardly produced on an industrial scale and only associated with a small number of available materials. Industrial data is not publicly available. This is also the case for the feedstock data of montmorillonite, which are based on a pilot plant. Processes that are not yet applied at industrial scale or were not found in the Econinvent database are described by simplified production process models, derived from encyclopedic knowledge. Data gaps exist and optimistic assumptions are made for intermediate process steps, with process efficiencies of 90%, efficient heating and water use, only partial estimates for impacts related to downstream processing and efficient recycling of solvents and surfactants. The latter may not represent industrial practice. Recycling of surfactants for LDH enables the comparison with the production of montmorillonite, for which an efficiency of organic modification of 100% has been assumed. The impact results indicate that heat and water use do not contribute largely to the final impact of the alternatives, but solvents have a high environmental impact. They are used in processes for *p*-hydroxycinnamic acid and Irganox 1010. The process chain leading to *p*-hydroxycinnamic acid is more complex (more process steps) compared to Irganox, which makes the results of *p*-hydroxycinnamic acid more uncertain. A comparison with the market prices of sodium stearate, Irganox 1010 and *p*-hydroxycinnamic acid indicates, however, that the NREU values are in the correct order of magnitude.
The assumption that the Wittig reaction is used for the production of *p*-hydroxycinnamic acid already leads to a contribution of 550 MJ NREU per kg of *p*-hydroxycinnamic acid, due to the Wittig reagent triphenylphosphine (TPPP). This is equivalent to 91 MJ/mole of *p*-hydroxycinnamic acid, which is in the same order of

magnitude as the impact of 117 MJ/mole as calculated for 1 mole of olefin, by Van Kalkeren et al.[64]. Theoretically it is possible to reduce the reaction product triphenylphosphine oxide (TPPO) to TPPP, and recycle it. An LCA has shown that the reduction of TPPO with the use of silanes lowers the environmental impact of the Wittig reaction.[64] Applying the impact reductions from that study, the NREU of *p*-hydroxycinnamic acid could be reduced from 1564 MJ/kg to 1200 MJ/kg. Nowadays, TPPO is still disposed of as waste.[65] P-hydroxycinnamic acid can also be obtained from fruit, which would make the impact of this material much lower. By analogy with the use of *p*-hydroxycinnamic acid as UV stabilizer in LDHs, also a (cationic) UV stabilizer could be found for MMT. However, the ionic exchange capacity of LDH (between 300 to 400 meq/100g) is higher than for MMT (around 100 meq/100g). Therefore LDH can contain more anions than the number of cations that can be intercalated in MMT. For a given level of UV stabilization, less LDH than MMT would hence be needed.

Comparing the LCA results on montmorillonite with other studies, different values are obtained for NREU and GHG emissions. The different values are given in Table 6. The inventory data for this study is based on the inventory data of Roes et al.[22], and the environmental scores are very comparable. The small difference may be caused by a different choice of background data. There are no details available on the inventory data of Joshi, so it is unclear what causes the difference in the results.

Table 6 Comparison of different studies concerning the environmental impact of montmorillonite

Study	NREU (MJ/kg)	GHG emissions (kg CO_2-eq/kg)
This study	72.8	3.25
Roes et al.[29]	69.7	3.55
Joshi[12]	40.1	1.52

Material properties

The amount of plastic needed to represent the functional unit is estimated using data on the tensile strength of LDPE and PBAT. However, the application of this method leads to uncertainties in the results because many values are reported for the tensile strength of LDPE, varying between 12 MPa[66] and 24 MPa[22]. This range has a very high influence on the outcome of the LCA. When 12 MPa is used for LDPE, the improvement in tensile strength is very large when PBAT is used (with a tensile strength of 45 MPa), which translates into a large reduction of film thickness. In this case, the environmental impact of films from petrochemical PBAT becomes lower than the impact of LDPE films that are first recycled and afterwards incinerated with energy recovery. Furthermore, the tensile strength values for PBAT are based on one experiment in the laboratory. To ensure the reliability of the results, the experiment should be repeated. It is also assumed that the tensile strength of PBAT with LDH/CO_3 has the same tensile strength as PBAT/LDH/stearate. A sensitivity analysis shows that if the LDH would not improve the film properties of PBAT, the impact of PBAT/LDH/stearate would be the same as the impact of PBAT/Irganox. For mulching films it could appear that the mechanical properties are not very important because the plants need to be able to break the films while they grow. UV stability is more relevant, as crosslinking due to photodegradation could make the film rigid, and thus more difficult to break. Beside UV stabilizers many other additives are used in general. These are excluded from this assessment.

In this study it was not possible to accurately account for the UV stabilizing properties of Irganox and *p*-hydroxycinnamic acid. 1 wt% of Irganox is added to the plastics and the amount of *p*-hydroxycinnamic acid in the nanocomposite is 1.5 wt%. However, the concentration of antioxidants in plastics is often only 0.1-0.5 wt%.[67] The molecular weight of Irganox 1010 (1178 g/mole) is higher than the molecular weight of *p*-hydroxycinnamic acid (164 g/mole), so the molarity of the latter is much higher, which could have a positive effect on the UV stability of the plastic. One should however note that Irganox 1010 has 4 functional groups (2,6-di-tert-butylphenol). A sensitivity analysis was performed for the case that only 0.5 wt% of Irganox 1010 is added to the polymer, and LDH with *p*-hydroxycinnamic acid is mixed with PBAT in the other alternative resulting in a molarity of *p*-hydroxycinnamic acid of 4 times the molarity of Irganox 1010. 5 wt% of LDH is obtained by addition of LDH/stearate. The tensile strength of PBAT mixed with both compositions of LDH is assumed to have the same value as PBAT with Irganox, which is a pessimistic estimate. In this scenario the NREU of the PBAT with LDH, UV stabilized by *p*-hydroxycinnamic acid, is only 3.1% higher than the NREU of PBAT with Irganox 1010, and only 1.1% higher than LDPE which is incinerated *without* energy recovery (which is a realistic scenario in many (European) countries where the recovery rate of plastic is far below 50%)[2]. If LDH based on magnesium oxide and aluminum hydroxide is used instead of LDH based on zinc chloride and aluminum chloride, these values reduce to resp. 2.2% and 0.2%. Already with a small (probable) improvement of the tensile strength due to LDH, the NREU of this alternative can be lower than of the LDPE and PBAT films without LDH. A study that includes the UV stability as a parameter could confirm this. The GHG emissions of LDPE are lower in every scenario, due to the high emissions related to the production of PBAT.

Practical application of recycling and incineration

Recycled LDPE has the lowest environmental impact among the different alternatives, but recycling of plastics brings practical issues. When extra UV stabilizers are added during recycling, attention should be paid to whether the concentration of UV stabilizers does not exceed (European) laws or regulations. Recycling plastic could be costly because of the recycling process and the labor required for collection and cleaning. If the collection of the waste is too costly and in absence of economic incentives, the farmer might not be motivated to participate in recycling or incineration with energy recovery.[1] If plastics are recycled it is important that the waste stream is homogeneous. Farmers could cooperate in waste separation and collection programs, such as a labelling scheme.[1] Not all the plastic is suitable for recycling. The quality has to be sufficient, even after photodegradation during the first use and storage period. The recycled plastic should be tested on, among others, tensile strength and elongation at break. Besides this, it is difficult to recycle thin films (*e.g.* mulching films). Contaminants are difficult to remove from the folds during washing, and water trapped in the folds is not easily eliminated. Films containing a high amount of pesticides could be qualified as hazardous, and should be handled correspondingly.[30] The substitution rate of recycled plastic, *i.e.* to what extent recycled plastic can replace primary plastic, is assumed to be 100%. Disregarding the practical issues of recycling, recycled LDPE is also favorable with a lower substitution rate, therefore a lower percentage would not influence the conclusion of this study.

Regarding incineration, a negative linear relation was found between the quantity of adhering soil and the calorific value of agricultural plastic waste.[30] The values for both parameters are obtained from this publication. For agricultural waste to be incinerated with energy recovery, the soil contamination must not exceed 50 wt% to maintain a good calorific value. As mulching films are known to be heavily contaminated with soil, attention should be paid to create clean waste streams.[30] If no credits are given for the incineration process, the NREU of PBAT with Irganox is the same as the NREU of LDPE with Irganox.

As not all the waste can be recycled or incinerated with energy recovery and farmers often do not cooperate with these disposal methods because of unawareness of the environmental consequences or high labor costs, most of the agricultural waste is being landfilled. This could result in aesthetic pollution, landscape degradation, threats to animals and blocking of water flows,[1] especially in the case of uncontrolled landfilling which is, as well as burning in the field, still practiced in some countries.[31]

So far only results for greenhouse gas emissions and non-renewable energy use have been discussed. To establish the impact of the different alternatives for further impact categories, an extra analysis was conducted, including landfilling. However, no further impact data is available for PBAT. Therefore, the analysis was performed only for LDPE/Irganox, incinerated without energy recovery, LDPE/Irganox recycled and afterwards incinerated without energy recovery, LDPE/Irganox which is being landfilled, LDPE/LDH/*p*-hydroxycinnamic acid, landfilled and LDPE/LDH/ZnAl-stearate, also landfilled. It is assumed that the tensile strength and other material properties are the same for all alternatives. The results are presented in Figure 14. For clarity the results of LDPE/LDH/*p*-hydroxycinnamic acid are omitted from the figure. This alternative has a much higher impact for all impact categories, except acidification. The impact on ozone layer depletion is extremely high for this alternative, due to the compounds lithium hydroxide and trichloromethane. A closer look into the (UV-stabilizing) material properties could significantly influence these results (see previous paragraph). Comparing the disposal options incineration and landfilling, landfilling has a higher impact in all categories, except global warming (due to the assumption of indefinite carbon storage in landfills). Compared to Irganox, LDH contributes more to ozone layer depletion and terrestrial ecotoxicity. Note that “landfilling” in the Ecoinvent database refers to organized municipal landfilling. If illegal landfilling takes place, the plastic could end up in the open nature, endangering animals, e.g. as marine debris[68], and food quality. Using biodegradable polymers could prevent this risk[69] and is therefore an important alternative, especially if the environmental impact of PBSF can be lower than LDPE if bio-based materials are used.

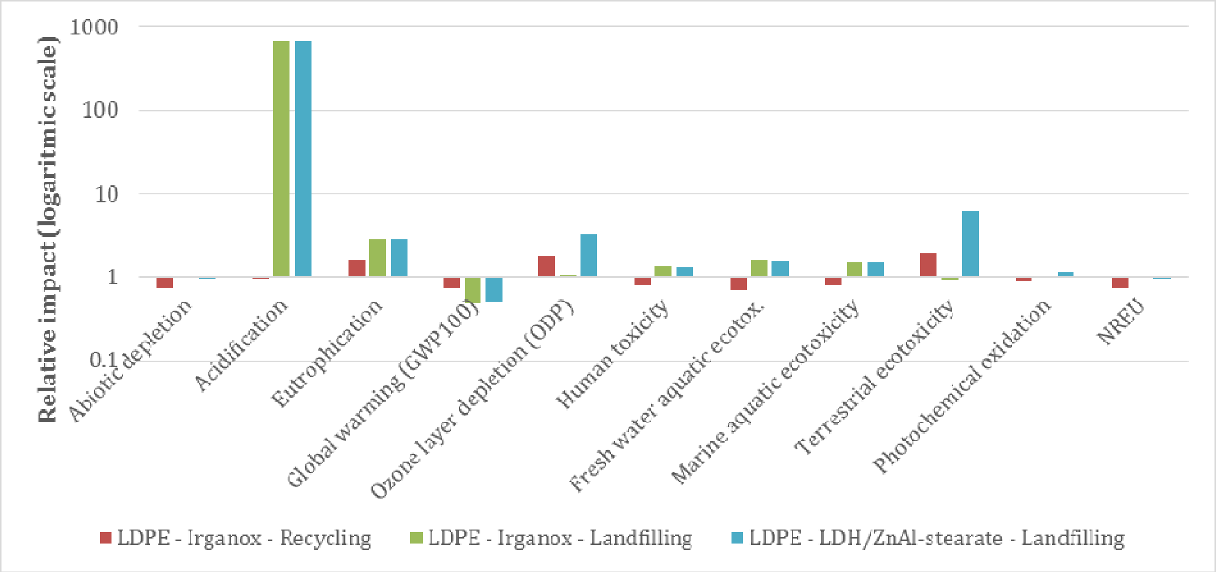


Figure 14 Analysis for further impact categories (besides greenhouse gas emissions and non-renewable energy use) and for a variety of product systems including landfilling. The results are presented relative to LDPE – Irganox – Incineration (index value = 1.0)

Toxicity

PBAT is a compostable polymer and for a material to be compostable, no toxic compounds must be present.[58] Toxicity is not included as an impact category in this LCA, due to the high uncertainty related to this impact category. However, given the relevance for this study, we assess toxicity in qualitative terms.

UV stabilizers and other additives are released into the environment by migration out of the polymer matrix,[7] and, in the case of biodegradable plastics, they are left in the field after the biodegradation of the polymers. As these additives are in general not biodegradable, it is possible that they accumulate in the environment and affect our health and the environment.[70]

Irganox 1010 is often used as UV stabilizer. It is not biodegradable, and it has potential to persist in the environment.[71] The Environmental Protection Agency[71] conducted a study on the toxicity of Irganox 1010. Irganox 1010 is a heavy molecule; therefore the uptake across biological membranes is limited which makes the potential of bioaccumulation low. Because of the low solubility in water, aquatic toxicity effects at high concentrations are assumed only to be physical (and not systemic). Human toxicity is classified as moderate, as fetuses of mice that were exposed to Irganox 1010 during the pregnancy had distinct deviations compared to the control group.[71] Although Irganox 1010 is not considered biodegradable, after 28 days 4-5% is degraded.[71] A study should be done on the products of this degradation, as these could be more harmful for the environment and human health because of the lower mass and potentially increased solubility in water. The behavior over a longer period of time should be studied by a multi-year test.

P-hydroxycinnamic acid can be found in various edible plants and it could degrade into CO and CO_2. However, *p*-hydroxycinnamic acid is known to be biologically recalcitrant due to its phenolic fraction; this makes the compound not easily biodegradable and it can inhibit the biological treatment of agricultural wastewaters.[72] The study of Mantzavinos et al.[72] is done with higher concentrations of *p*-hydroxycinnamic acid (738 mg/l) than relevant for this study (190 mg/m^2/year). Another study indicates a readily biodegradability of the phenolic compounds of *p*-hydroxycinnamic acid in the soil.[73] Also the intermediate compounds are easily biodegradable.[72] A toxicity review presents no evidence associating cinnamic acid or its related compounds to any toxic threat.[74] P-hydroxycinnamic acid could even have positive effects on human health due to its antioxidant effect.[75]

Nanoparticles are released to the environment after the biodegradation of PBAT containing LDH, or potentially (in reduced amount) after incineration of LDPE containing nanoparticles. Depending on the nanocomposite materials, it could be an option to recycle the nanocomposites and to separate and reuse the nanofillers.[76] However, not much is known about this last option. Incineration of nanocomposites is not investigated as a disposal option in this study, but it will be covered in this section due to the relevance of this option. Wohlleben et al.[76] show that during the use phase of nanocomposites no nanoparticles are released, but this not the case for biodegradable nanocomposites as the (non-biodegradable) nanoparticles are left in the field. These nanoparticles could leach into the groundwater, and subsequently into drinking water. There is also a chance that they end up in the food chain.[77]

Free nanoparticles can have a negative impact on the environment and human health, due to their toxicity, persistence in the environment and bioaccumulation. The risks associated with one-dimensional (asbestos-like) nanoparticles could in this case be limited by the fact that the nanoparticles from this study are two-dimensional platelets. Nanoparticles can enter the human body by inhalation, ingestion and absorption through the skin, where they could damage the immune system, the brain and the nervous system. They have shown respiratory toxicity, cardiovascular toxicity and cytotoxicity. Besides this, nanoparticles appear to exhibit ecotoxicity. Nanoparticles containing zinc and aluminum, as used in this study, appeared to be toxic to the germination and growth of roots in the seedlings of several agriculturally relevant plants.[77] An extensive overview on the effects of free nanoparticles on human health and ecotoxicity can be found in the publication of Roes et al.[77]. Due to processes such as redox reactions, interactions with organic macromolecules or cellular material, dissolution or adsorption of known pollutants, nanoparticles can change their surface chemistry and consequently their transport and exposure routes. Besides this, organisms could influence nanoparticles, for example by stabilizing them.[78]

When nanocomposites are incinerated the nanoparticles can be destroyed, but also (secondary) nanoparticles can be released with the fly ash and/or the off-gas. Depending on the off-gas treatment, particles can be captured before the release in the environment. However, for nanoparticles smaller than 100 nm, the efficiency to capture nanoparticles is often not higher than 80%.[77] As these particle-capturing solutions could be energy intensive, they should be included in the LCA. Nanoparticles that stay attached to the solid residues after incineration can end up in landfills which are used as new material resources, and released into the air in later processing.[79]

According to the European Community Regulation REACH (Registration, Evaluation, Authorisation and Restriction of Chemical substances), nanomaterials require a risk assessment, performed on a case-by-case basis.[80] Roes et al. propose laboratory experiments to test the incineration and off-gas removal of the nanoparticles, and *in vivo* tests to determine the toxicity of the released nanoobjects.[77] As long as the fate of the nanoparticles and the potential risks are unknown, the precautionary principle should be applied.[79]

In the case that surfactants are included in the nanocomposites, it should be noted that besides the harm caused by the nanosize of the material, organo-modified clay also releases toxic compounds during processing and storage.[81] This can be prevented by using different processing techniques which do not require the addition of surfactants.[82]

Another point not addressed here is the interaction between the components in a complex system as studied here (inorganic platelets, the organic molecule and the polymer). Over time, this might yield (toxic) substances through chemical or photo-chemical reactions, potentially catalytically enhanced in presence of the sun, oxygen molecules and moisture.

Conclusions

In this study an *ex-ante* Life Cycle Assessment was prepared to assess and compare the environmental performance of several material compositions and disposal options for agricultural mulching films. The biodegradable polymer PBAT, with and without nanoclay, is compared with LDPE that is recycled and incinerated with energy recovery. Different types of nanoclays are compared, as well as the UV stabilizers Irganox 1010 and *p*-hydroxycinnamic acid. Among the nanoclays the lowest environmental impact is achieved in the case of layered double hydroxides (LDH) based on magnesium oxide/hydroxide and aluminum oxide/hydroxide, with the surfactant stearate as intercalated anion. For the mulching films the lowest NREU and GHG emissions are obtained when films are made of LDPE, which is recycled and after the second life cycle incinerated with energy recovery. LDPE is in general favorable over petrochemical PBAT, due to energy credits that are given in the incineration process. PBAT containing LDH with the surfactant stearate has a slightly lower impact than PBAT without LDH, because of the improvement in the tensile strength. The PBAT nanocomposite with LDH and the UV stabilizer *p*-hydroxycinnamic acid has a higher impact than the other alternatives, due to the high impact of *p*-hydroxycinnamic acid. However, this alternative could be more interesting than LDPE when PBAT is made of bio-based feedstock (resulting in "PBSF") and when the UV stability is regarded as critical parameter. In that case part of the LDH/*p*-hydroxycinnamic acid could be replaced by LDH/stearate, which could even lead to a lower use of PBAT or PBSF due to improved material properties. However, the lack of recycling and energy recovery in many geographical areas and the impacts and risks associated with (illegal) landfilling make the alternatives based on biodegradable PBAT favorable already today. Further environmental benefits can be achieved by using *p*-hydroxycinnamic acid instead of Irganox 1010 due to the toxicity and lack of biodegradability of Irganox 1010. In order to complete the analysis the toxicity of the nanoparticles that are left in the field should be assessed; this calls for further research.

This study focusses on the commercially available biodegradable PBAT and its direct bio-based alternative poly(butylene succinate-co-butylene furandicarboxylate) (PBSF). However, other bio-based polymers are already more developed than PBSF, such as polybutylene succinate (PBS). PBS could also be used for LDH/polymer nanocomposites, where the inorganic platelets are organo-modified by surfactant molecules[83] or fatty acids[84]. Even starch could be used to incorporate LDHs[85]. These other material compositions fall however outside the scope of this study.

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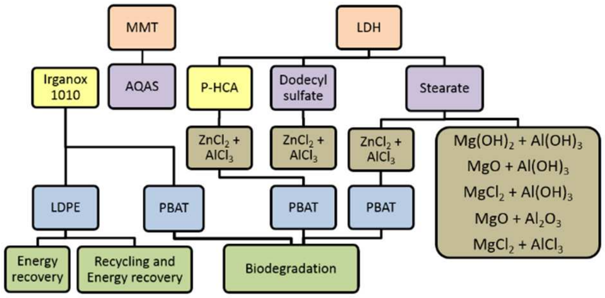
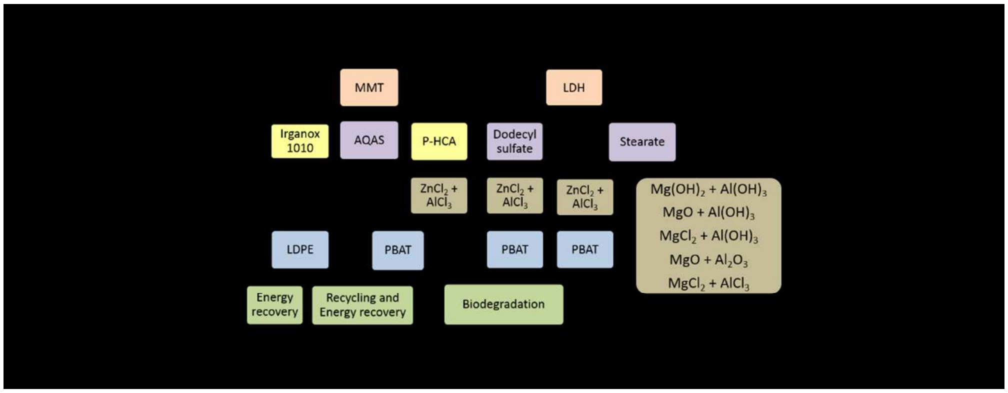
Table of Contents

New layered double hydroxide nanoclays are assessed, considering the UV stability of polymers and their nanocomposites.





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