



# Impact of nanoparticles on the environmental sustainability of polymer nanocomposites based on bioplastics or recycled plastics – A review of life-cycle assessment studies

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## ABSTRACT

Adding nanoparticles to a host polymer can lead to performance improvements that can be twice as beneficial to the environment: first, sustainable nanocomposites based on bioplastics or recycled plastics could replace ubiquitous petroleum-based polymers; second, substantial plastic saving could be achieved by profiting from the superior specific properties of the nanocomposites. Nevertheless, the inherent environmental burden of nanoparticles can compromise the expected benefits. Here we address the controversial issue of the environmental sustainability of "green" polymer nanocomposites based on bioplastics and recycled plastics. A critical review of life-cycle assessment studies regarding nanocomposites and their individual constituents is presented. Nanoparticles have a remarkable environmental impact despite their typically low content. Except for organo-clays and graphene, the production of common nanofillers (nanocellulose, titanium dioxide, silver and, above all, carbon nanotubes) emits relevant amounts of greenhouse gases and requires high energy, nullifying the advantages of using green polymer matrices. Reaching high performance becomes hence crucial to make polymer nanocomposites truly sustainable through material saving. For this purpose, increasing the content of nanoparticles or functionalizing them to enhance their dispersion in the host polymer can unexpectedly entail environmental benefits.

## 1. Introduction

The End-of-Life options for plastics products have been neglected in the past, and because of their extremely high resistance to degradation in natural environments, plastics have massively accumulated in the aquatic and terrestrial ecosystem (Geyer et al., 2017; Kaur et al., 2018). Even with immediate and concerted actions, hundreds of million metric tons (Mt) of plastic waste are predicted to accumulate in the environment in the coming decades (Lau et al., 2020). To limit this trend, coordinated global actions are needed to reduce plastic consumption, increase the rate of reuse and recycling, and accelerate innovation in the field of sustainable substitute materials. While the first two points mainly rely on consumer education and awareness, polymer scientists

play a major role in proposing ecofriendly alternatives to ubiquitous petroleum-based plastics. Bioplastics (bio-derived and/or biodegradable) and recycled plastics could be excellent candidates, but their properties are often below expectations. As a result, the global employ of all plastics produced worldwide. A possible strategy to reverse the trend is adding nanoparticles, which are known to enhance many technological properties of a host polymer matrix (Fu et al., 2019). Numerous studies have been carried out in the last decades looking for optimized formulations of green polymer nanocomposites (PNCs) based on bioplastics (Adeosun et al., 2012; Arjmandi et al., 2017; Modi et al., 2015; Pandey et al., 2005; Ray and Bousmina, 2005; Thakur et al., 2017) or recycled plastics (Chen and Ahmad, 2017; Khan et al., 2014; Mahanta et al.,

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2012; Mallakpour and Behranvand, 2017; Uddin et al., 2020; Zare, 2013), but unless few notable exceptions (Civancik-Uslu et al., 2018; Joshi, 2008; Lambert and Wagner, 2017), the attention of the scientific community has been largely focused on the performances. The actual sustainability of this new class of materials has been guiltily neglected. The last review articles that analyze the state of the art on this topic date back to 2008 and 2013 (Joshi, 2008; Kim and Fthenakis, 2013), and a more recent review by Civancik-Uslu et al. mainly regards micro-sized fillers and fibers (Civancik-Uslu et al., 2018). Here we aim at filling this gap, performing a thorough review of the literature concerning the environmental impact of PNCs based on bioplastics and recycled plastics. The goal is providing quantitative information to be used as a guideline for a correct selection of materials and processes to produce truly sustainable PNCs. Therefore, the analysis is restricted to studies in which the impact of green PNCs and their single constituents, i.e. green polymers and nanoparticles, is quantitatively estimated through standardized life-cycle assessment (LCA). The latter is a widely recognized methodological framework for assessing the environmental impacts and the resources used throughout the whole lifecycle of a certain product, from raw material acquisition, via production and use phases, to waste management, including disposal and recycling (Finnveden et al., 2009). When such a holistic approach is adopted, materials mistakenly perceived as eco-friendly can result more impacting than others with worst reputation. As an example, petroleum-based polyolefins with well-established recycling technologies can result more sustainable than “green” biopolymers such as poly(lactic acid) (PLA) and polyhydroxyalkanoate (PHA), which pay the price of fertilizers used to grow the corn they are derived from (Tabone et al., 2011).

Since the pioneering studies by Angelini and Lloyd and Lave in 2003 (Angelini et al., 2003; Lloyd and Lave, 2003), a surprisingly low number of papers dealing with the LCA of PNCs has been published to date. A Scopus search for papers containing both “LCA” AND “nanocomposites” in title, abstract, or keywords returns less than 50 documents, which further reduce after refining the search ([www.scopus.com](http://www.scopus.com), accessed in November 2021). Only a dozen of papers specifically addresses PNCs based on bioplastics or recycled matrices. Things change when the search is performed by combining “LCA” and the single constituents of green PNCs, i.e. “bioplastics”, “recycled plastics”, and “nanoparticles”: the number of documents per year is significantly higher and exhibits a growing trend, with an exponential increase in the last two decades. This proves a generalized interest towards eco-sustainability issues, although, to date, most of the LCA studies remained focused on basic systems and raw materials. Aiming at expanding the basis of our analysis, here we also review the literature regarding the single constituents of green PNCs, namely bioplastics/recycled plastics and nanoparticles. In this way, general conclusions about the sustainability of green PNCs in terms of raw materials can be obtained by assuming a simple additivity rule. The manuscript, meant for polymer scientists and engineers from both academia and industry who are not necessarily experienced in the field of LCA, is structured as follows:

- in Section 2, the literature on LCA studies on PNCs is thoroughly reviewed. Both cradle-to-gate and cradle-to-grave studies are considered. Papers on non-green PNCs are not neglected (subsection 2.1), as they provide useful information on the impact of nanoparticles and compounding process irrespective of the green feature of the matrices. Emphasis is put on the global warming potential (GWP) and non-renewable energy use (NREU), which are the most addressed impact categories in LCA studies.
- In Section 3, the literature concerning LCA studies on green polymers (subsection 3.1) and nanoparticles alone (subsection 3.2) is reviewed to highlight the factors that mostly contribute to the environmental impacts of the constituents of green PNCs. Major attention is paid to the impact of nanoparticles, with specific paragraphs dedicated to the main classes of nanoparticles used in PNCs (clay, CNTs, graphene, nanocellulose, TiO<sub>2</sub>, and Ag). Only cradle-to-gate analyses

are considered in this section, as the goal is collecting information on the phases of raw material acquisition and manufacturing.

- Finally, in Section 4 the data collected in Section 3 are elaborated by resorting to a simple additivity rule to infer the environmental impact of typical PNCs, i.e. PNCs based on green matrices and containing typical amounts of the various classes of nanoparticles. This leads to the ultimate goal of our study, which is providing researchers and manufacturers with useful information for an informed selection of polymers, nanoparticles and processes for producing truly sustainable PNCs.

## 2. Sustainability of polymer nanocomposites (PNCs)

The attention of scientific community on PNCs was initially driven by the enhancement of the performance. The environmental implications were guiltily neglected for at least a decade. Only few authors recognized the environmental merits of PNCs, whose excellent specific properties can lead to considerable material saving at equal performances (the so-called “functionality-based approach”). Another environmental advantage of using nanoparticles is the possibility of valorizing sustainable matrices such as bioplastics or recycled plastics, whose scarce performances prevented their use as substitutes of petroleum-based products. The other side of the coin is the environmental impact of nanoparticles: even if added at very small amounts, the energy and resources required for their synthesis, modification and compounding with the host polymers (not to talk of their potential toxicity) bring about a negative impact that could compromise the overall sustainability of PNCs (Kim and Fthenakis, 2013). The environmental pros and cons of PNCs are discussed in detail below, where a selection of noteworthy LCA studies on PNCs is reviewed. Historically, the first studies dealt with PNCs based on non-green matrices. For this reason, we begin with a short review of this class of PNCs (subsection 2.1), and then we move to green PNCs (subsection 2.2). The reviewed papers, collected with Scopus searching for documents having “LCA” AND “Nanocomposite” in title, abstract or keywords, are listed in Table 1 together with useful additional information, such as the product/application the PNCs are intended for, the system boundaries, and the end-of-life options and impact categories analyzed in the original paper.

### 2.1. Non-green PNCs

Lloyd & Lave addressed the environmental implications of replacing conventional steel with organoclay-filled polypropylene (PP) in motor vehicle body panels (Lloyd and Lave, 2003). The authors used the Ashby’s stiffness index  $M = E^{1/3}/\rho$  (where  $E$  is the tensile modulus and  $\rho$  is the density) (Ashby, 1994) to estimate the weight reduction achievable by using PNCs. Significant reductions in both fuel consumption and CO<sub>2</sub> emissions were assessed (up to 8.1% of CO<sub>2</sub> equivalent saved for a 1-year fleet of 16.9 million of vehicles in the United States). This was presented as a general principle in the automotive sector, in which the greenhouse gas emission related to the material production phase is negligible compared to that of petroleum production and vehicle use. Therefore, each scenario of metal substitution with lighter materials such as PNCs results in lower GWPs.

Although reasonable, the conclusions by Lloyd & Lave suffer from the lack of specific data on the impacts of nanoclay manufacturing and incorporation in the host polymer. This crucial aspect was highlighted by Khanna and co-workers, who identified the carbon nanofibers (CNF) production as the most energy-intensive step of the manufacturing process of thermoplastic (PP) and thermoset (unsaturated polyester) nanocomposites for car body panels (Khanna et al., 2008, 2012). Since this energetic burden was found to overcome the fuel savings deriving from weight reduction, the selected PNCs turned out not convenient as substitute for steel. Similar conclusions were also drawn regarding greenhouse gas emissions.

**Table 1**

List of LCA studies on PNCs. Information on materials, production and main features of the LCA analyses is reported for each document.

Ref.	Materials and production				Product/Application	System boundaries	LCA	
	Recycled	Polymer(s)		Nanoparticles <sup>(1)</sup>			End-of-Life <sup>(2)</sup>	Impact categories <sup>(3)</sup>
		Bio-based	Non-green					
Lloyd and Lave (2003)			PP	Clay	Motor vehicle body panels/Automotive	Cradle-to-grave	L	C; A; R.f; W; R.m&m; L; TT
Khanna et al. (2008)			PP	CNF	Car body panels/Automotive	Cradle-to-grave	–	R.f
Khanna et al. (2012)			PP	CNF	Car body panels/Automotive	Cradle-to-grave	–	C; R.f
Roes et al. (2010)		Various, both green and non-green		Clay; SWNT; MWNT; Si; CaCO <sub>3</sub>	Panels	Cradle-to-grave	T	NREU
Roes et al., (2007a)			PP; PE; fiber-reinforced PP	o-Clay	Thin film/Packaging; thick film/Agriculture; Injection molded panels/Cars	Cradle-to-grave	T	C; A; E; OF; OD; NREU
Pizza et al. (2014)			Epoxy	GnP	Thermal interface materials/Electrotechnical industry	Cradle-to-grave	L, T	C; A; ET.w; E.m; E.w; OF; W; R.m&m; R.f; OD; HW
Westerband and Hicks (2018)			HDPE	nAg	Food packaging	Cradle-to-grave	L	C; A; OD; E; OF; HT.c; HT.nc; R.f
Hervy et al. (2015)			Epoxy	BC; NFC		Cradle-to-grave	L	C; A; R.f; OF; ET.w
Pietrini et al. (2007)		PHB	PP	Clay	Catode ray tube monitor housing/Electronic industry; internal car panels/Automotive	Cradle-to-grave	C	C; NREU
Roes et al., (2007b)		PHB	PP	Clay	Film/Packaging, Agriculture; Catode ray tube monitor housing/Electronic industry; internal car panels/Automotive	Cradle-to-grave	C	C; NREU
Schrijvers et al. (2014)		PBAT		LDH	Mulching Films/Agriculture	Cradle-to-grave	C	C; NREU
Petrucci et al. (2018)		PLA		CNC, Clay	Film/Packaging	Cradle-to-grave	C	C; A; E; OD; HT.c; HT.nc; ET.w; R.m&m; R.f; L; I
Cinelli et al. (2017)		PLA		ChNF	Nanocomposite masterbatches/Packaging	Cradle-to-grave	C	C; A; E; E.w; P; OF; OD; HT.c; HT.nc; ET.w; L; I
Lorite et al. (2017)		PLA		Clay	Food container/Packaging	Cradle-to-grave	C, T, L	C; A; E; E.w; P; OF; OD; HT.c; HT.nc; ET.w; ET.w; R.m&m; R.f; L; I
Nguyen et al. (2017)	HDPE		HDPE	Clay	Pipes/Drainage pipe industry	Cradle-to-grave	–	C; NREU
Nguyen et al. (2020)	HDPE	bio-HDPE	HDPE	Clay	Pipes/Drainage pipe industry	Cradle-to-grave	L, T, R	C

<sup>1</sup> Organo-modified clay (Clay); Single-walled nanotubes (SWNT); Multi-walled nanotubes (MWNT); nanosilica (Si); Carbon Nanofibers (CNF); Calcium Carbonate (CaCO<sub>3</sub>); Graphite nanoplatelets (GnP); Bacterial nanocellulose (BC); Nanofibrillated cellulose (NFC); nano silver (nAg); layered double hydroxides (LDH); Cellulose nanocrystals (CNC); Chitin Nanofibrils (ChNF).

<sup>2</sup> Recycling (R); Thermo-valorization (T); Landfilling (L); Composting (C).

<sup>3</sup> Climate change (C); Acidification (A); Eutrophication (E); Eutrophication, terrestrial (E.t); Eutrophication, marine (E.m); Eutrophication, freshwater (E.w); Particulate matter (P); Photochemical ozone formation (OF); Human toxicity, cancer (HT.c); Human toxicity, non-cancer (HT.nc); Ecotoxicity, freshwater (ET.w); Water use (W); Resource use, minerals and metals (R.m&m); Resource use, fossils (R.f); Ozone depletion (OD); Land use (L); Ionizing radiation (I). Non-renewable energy use (NREU); Total toxic releases (TT); Hazardous waste (HW).

The cruciality of weight savings in case of PNCs also emerged in (Roes et al., 2007a; Roes et al., 2010), where LCA (cradle-to-grave) and Life Cycle Costing (LCC) methodologies were applied to packaging films, agricultural films, and automotive panels. Appreciable environmental and economic benefits were only achieved in agricultural films, where a 36.5% weight saving was proven possible by replacing conventional polyethylene (PE) with a PP-based nanocomposite. In contrast, the ratio between weight saving and environmental costs of producing nanoparticles and adding them to the host polymer resulted unfavorable in the other two applications.

Mechanical properties are not the only ones that benefits from the use of nanoparticles. Pizza et al. analyzed thermally conductive epoxy-based systems loaded with 5.8 wt% of graphite nanoplatelets (GNPs) for electrotechnical applications (Pizza et al., 2014). Raw materials extraction and filler and resin preparation accounted for most of the overall impact, with high energy consumption (308 MJ kg<sup>-1</sup>) and GWP (15.7 kg CO<sub>2</sub>-eq. kg<sup>-1</sup>). It is worth noting that contributions related to the nanoparticles often surpassed those of the epoxy matrix. The GNPs,

however, ensured excellent thermal conductivity (1 W/mK for PNC vs. 0.2 W/mK for neat epoxy), making the PNC preferable in high technological value sectors, such as aeronautics or aerospace.

To conclude this brief survey of the LCA studies on non-green PNCs, we observe that some papers addressed systems with an improved ecological footprint due to the use of bioderived nanofillers. Among others, Hervy et al. evaluated the environmental impact of an epoxy composite reinforced with bacterial nanocellulose (BC) or nanofibrillated cellulose (NFC) (Hervy et al., 2015). Neat PLA and GF/PP were chosen as benchmark materials, and the comparisons were made in terms of the Ashby's stiffness index. When considering the manufacturing phase, the environmental footprint of the PNCs resulted much higher than that of the reference systems because of the high environmental impact of cellulosic nanoparticles (see also Section 3.2). When the analysis was extended to the whole life cycle, the environmental impact of the NFC/epoxy approached that of GF/PP, which remained the best performing system. The authors predicted that an increase in the elastic modulus achievable at nanoparticle contents

higher than those investigated could lead to further environmental benefits thanks to material savings, but such a conjecture remained unproved.

## 2.2. Green PNCs

Nine out of fifteen LCA studies on PNCs regard systems based on bio-based plastics, which are expected to be more sustainable than petroleum-based ones. Pietrini et al. made a comparative analysis considering poly(hydroxybutyrate) (PHB) and PP nanocomposites filled with organo-modified clays for cathodic-ray tubes (CRT) monitor housing and automotive panels (Pietrini et al., 2007). Following the same approach of former studies (Roes et al., 2007b), the authors demonstrated that PHB suffers from its relatively low Young's modulus and high density, which imply the use of more material for the same application. Such a disadvantage, however, is offset by the benefits arising from the saving inputs in the PHB production process. As a consequence, PHB resulted environmentally preferable to PP for both applications in a cradle-to-factory gate framework, performing better than PP for CRT monitor housing in a cradle-to-grave one. However, this conclusion suffers from the lack of reliable data for PHB production at industrial scale.

In a subsequent paper, the same authors systematized the approach for a large set of PNCs based on both petrochemical and bio-based thermoplastic and thermoset matrices filled with montmorillonite clay, silica, CaCO<sub>3</sub>, and single- and multi-walled carbon nanotubes (Roes et al., 2010). NREU data, considered as a good indicator for many environmental indices, were divided by the Ashby's material indices for stiffness and strength to get a "functionality-based NREU". The latter parameter was found to decrease with filler content for most of considered samples (15 out of 19; Fig. 1). This means that, in general, the increase of mechanical properties offsets the environmental impact of nanoparticle production. Increasing NREU values with filler content were ascribed to a high variability of the available data, often referring to early lab-scale production technologies. In this regard, the authors concluded that lower life cycle impacts are expected in the near future thanks to technological advances.

Some studies on green PNCs refer to applications in the agricultural and packaging sectors, in which the use of sustainable polymers can lead to immediate advantages due to large market volumes and short product lifecycle. LCA of nanocomposites for agricultural films was investigated, among others, by Schrijvers et al. (2014). They focused on biodegradable poly(butylene adipate-co-terephthalate) (PBAT) filled with layered

double hydroxides (LHD) and functionalized with two UV stabilizers, one commercial and the other natural. PBAT and conventional low-density PE (LDPE) films functionalized with the commercial UV stabilizer were taken as reference. The authors used Ashby's material indices to compare the properties of the different systems. Considering that LDH nanocomposites are still in a prototyping phase, much of the data referred to a laboratory scale and were scaled up to an industrial level. The impact categories were NREU and climate change in terms of greenhouse gas emissions (GHG). In a cradle-to-grave framework, conventional LDPE-based films were found to have lower impact than PBAT-based ones. This was ascribed to energy credits of LDPE from its incineration at the end of its service life, as well as to lower GHG emissions related to LDPE production process. The lowest impact was calculated for LDPE systems containing the commercial UV stabilizer, then recycled after the first use, and finally incinerated after the second use. This scheme led to GHG of 600 kg CO<sub>2</sub>-eq. and NREU close to 10,000 MJ. Among the PBAT films, the nanocomposites containing LDH performed slightly better due to improved material properties, with a final GHG slightly lower than 900 kg CO<sub>2</sub>-eq. and NREU close to 12,000 MJ.

Recently, Petrucci et al. performed a comparative cradle-to-factory gate analysis on a PLA/cellulose nanocrystals/limonene system, taking a PLA/organo-modified montmorillonite system with a petroleum-based plasticizer as benchmark (Petrucci et al., 2018). The green PNC performed better than the reference system in almost all the examined impact categories. Environmental benefits of green PNCs for packaging were also reported by Cinelli et al., who performed a preliminary LCA analysis of PLA blends containing chitin nanofibrils (Cinelli et al., 2017). Lorite et al. performed a detailed LCA investigation on a PLA-based nanocomposite for active packaging, going beyond the factory gate (Lorite et al., 2017). The authors found that the manufacturing phase was the main responsible for the environmental impact, followed by the material production and transportation phases. Compared to PET packaging, the green PNC resulted more energy-consuming and impacting on ecosystem quality (i.e., aquatic eutrophication and land occupation), but they resulted less harmful to human health (i.e., carcinogens and non-carcinogens) and turned out to be able to extend the shelf-life of the packed foods by ~30%.

Green PNCs based on recycled plastic have received scarce attention in the literature. In the authors' opinion, greater efforts should be made to investigate the sustainability of this class of matrices, as the reuse of already available plastics could be preferable to the production of new (albeit green) plastics. In this context, two papers by Nguyen et al. investigated the potential of PNCs based on recycled matrices. In a first study, the authors performed a cradle-to-gate LCA study and a cost analysis on three systems for drainage pipe applications based on virgin high-density PE (HDPE), a blend of virgin and post-consumer recycled HDPE (HDPE/PCR), and HDPE/PCR nanocomposites containing up to 6 wt% of nano-clays (Nguyen et al., 2017). Producing nanocomposite pipes based on a (partially) recycled matrix ensured a decrease in greenhouse gas emissions due to the minimal dependence on the crude oil extraction and processing stages. The nanocomposite pipe was also lighter than the conventional material, with obvious advantages in terms of cost and the energy consumed during installation and transportation. Moreover, the manufacturing cost of HDPE/PCR nanocomposite pipes was ~17% lower than that of virgin HDPE pipes, which proves that the production costs of nanoparticles can be offset by the gain resulting from the replacement of part of the virgin polymer with recycled polymer. In a subsequent paper, the same authors included in their comparison also bio-based HDPE (bio-HDPE) pipes and extended the analysis to a cradle-to-grave framework (Nguyen et al., 2020). When considering the entire service life, mechanical properties become the discriminating parameter. In this new scenario, the worst properties of pipes containing recycled HDPE resulted in the need for more material per pipe compared to the reference system based on virgin HDPE. However, nanoparticles were predicted to slow down the growth rate of

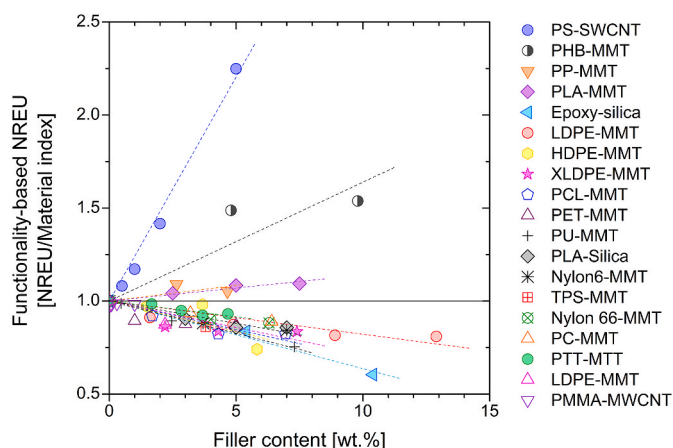


Fig. 1. Functionality-based NREU data to produce PNC panels at different nanoparticle content with stiffness-limited design. "MMT" stands for montmorillonite, "MWCNT" and "SWCNT" stand for multi-walled and single-walled carbon nanotubes, respectively. Readapted from (Roes et al., 2010) with copyright permission of Springer Nature.

cracks generated during service life. This should allow for a mass reduction and, through it, to a decrease in the environmental impact of nanocomposite pipes containing recycled HDPE. The latter resulted advantageous also in terms of production costs, confirming that nanocomposite pipes partially based on recycled plastics represents an environmentally and economically sustainable alternative to conventional HDPE pipes.

### 3. Sustainability of green PNC components

To go beyond the limited literature on LCA of PNCs, the environmental sustainability of their single constituents, i.e. green polymers and nanoparticles, is discussed in this Section. First, we briefly recall some general conclusions on the impact of green matrices, which are addressed in many focused articles and reviews. Greater attention is paid to the environmental impact of nanoparticles, which are responsible for a considerable fraction of the overall impact of PNCs. All the following considerations refer to cradle-to-gate studies, and the collected data are used in Section 4 to predict the overall impact of the production phase of green PNCs.

#### 3.1. Bioplastics and recycled plastics

Whether bioplastics are more sustainable than fossil-based ones is still an open issue. In contrast with the common feeling, two recent reviews question the superiority of bioplastics, showing that their impact in terms of climate change and energy use is comparable with that of conventional plastics (Kakadellis and Harris, 2020; Walker and Rothman, 2020). A collection of cradle-to-gate data on greenhouse gas emissions and energy demand for biopolymers is reported in Fig. 2 (open symbols; numerical data and references are listed in Appendix A, Table A1). 75% of the points fall in the range  $0 \div 3 \text{ kg CO}_2\text{-eq. kg}^{-1}$  (GWP) and  $20 \div 80 \text{ MJ kg}^{-1}$  (NREU), in line with petroleum-based plastics. The gap with the latter would further reduce by removing questionable  $\text{CO}_2$  credits often assigned to bioplastics, and by considering social and ethical issues emerging when using agricultural feedstocks for producing bioplastics (Chaplin-Kramer et al., 2017; Spierling et al., 2018).

The use of recycled plastics implies obvious environmental and economic benefits deriving from reusing already available materials. On the other hand, the additional processing steps needed to collect, sort and re-process plastic wastes and scraps bring non-negligible environmental burdens that could offset the credits. The evaluation of the environmental impact of second-life materials such as recycled plastics is a complex matter, and the related literature is quite poor and often

controversial (Perugini et al., 2005; Gu et al., 2017; Rajendran et al., 2012, 2013). The shortage of literature reflects the limited palette of actually recyclable plastics (essentially PET and HDPE), while the variability of the numerical data on energy consumption and greenhouse gas emissions is due to ambiguities on the allocation of the environmental impact of the virgin materials from which recycled plastics are derived. Shen et al. compared different allocation methods and provided a rich set of data on recycled PET (Shen et al., 2012). This dataset has been averaged and is shown as full circles in Fig. 2. The full triangle in the same plot generically refers to typical recycled plastics and is taken from (Hopewell et al., 2009).

The few available data suggest that the environmental impact of recycled plastics is slightly lower than that of bioplastics in terms of NREU, but higher for what concerns greenhouse gas emissions. This is likely due to the  $\text{CO}_2$  credits often ascribed to biopolymers obtained from plants or algae. The preferability of recycled plastics over other green matrices strongly depends on their performance. Re-processing can cause significant drops in the properties of recycled plastics. The addition of fillers and additives could balance this loss (Al Ma'adeed et al., 2011), but such a strategy brings about an environmental burden. In particular, impact modifiers, largely employed for toughening purposes, can significantly raise the environmental footprint of recycled plastics (Gu et al., 2017).

#### 3.2. Nanoparticles

Although nanoparticles represent the minority component of PNCs, their synthesis and surface modification can be very costly from the environmental point of view, possibly compromising the overall sustainability of green PNCs. The literature of LCA on nanoparticles is much more abundant than that found for PNCs. A Scopus search for "LCA" AND "Nanoparticle(s)" in title, abstract and keywords returns about 175 documents since 2006. To meet the purposes of this study, we restricted the analysis to the nanoparticles most commonly used for PNCs, i.e. organoclays, carbon-based nanoparticles (carbon nanotubes (CNTs) and nanofibers (CNFs) and graphene-like nanoparticles), nanocellulose (NC), titanium dioxide ( $\text{TiO}_2$ ) and silver (Ag). Moreover, papers focused on niche applications were neglected. Finally we get about 40 papers, which are listed in Table A2 (Appendix A) together with bibliographic references and information on the synthesis procedure. The values of GWP and NREU are summarized in Fig. 3. Significant variability of data can be noticed. One reason relies on the different synthesis routes, which can be divided into chemical (e.g., CVD, reduction, extraction, hydrolysis, hydrothermal processes) and physical methods (e.g., arc discharge, plasma, spark method, flame spray pyrolysis, ultrasonication). Another source of variability of NREU and GWP data is the yield of the various process, which can vary a lot, especially in relation to the quality of the nanoparticles to be synthesized. In particular, for CNTs, the higher the quality of the nanoparticles (CNT length, structural regularity, purity, etc.), the lower the yield (Upadhyayula et al., 2012). Since LCA accounts for all energy and materials used to produce reagents, including those that are used in excess (Pati et al., 2014), data for energy consumption and emissions can vary by orders of magnitude even for the same type of nanoparticles.

##### 3.2.1. Organically modified clays

Only few studies addressed the environmental impact of nanoclays, which were the first and probably the most studied class of nanoparticles for realizing PNCs. Moreover, none of these papers strictly focuses on the nanofiller, being rather aimed at estimating the environmental impact of clay-based PNCs on the whole. In the field of PNCs, the term "nanoclay" indicates the family of layered silicates clays such as montmorillonite, hectorite, and saponite. These are 2:1 phyllosilicate in the form of  $\sim 1 \text{ nm}$ -thick silico-aluminate layers piled together to form stacks. In a well-dispersed PNCs, the polymer penetrates the inter-layer galleries, distancing the layers or isolating them (Kotal and Bhowmick, 2015). For

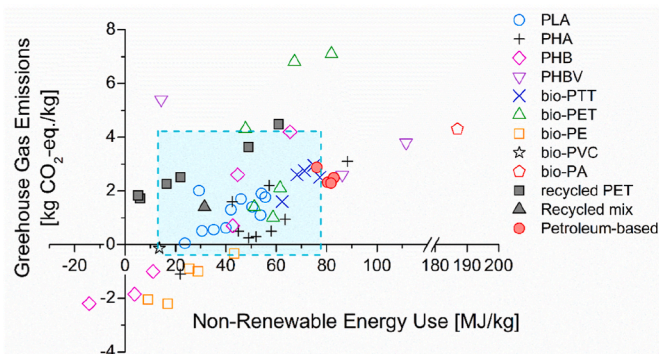
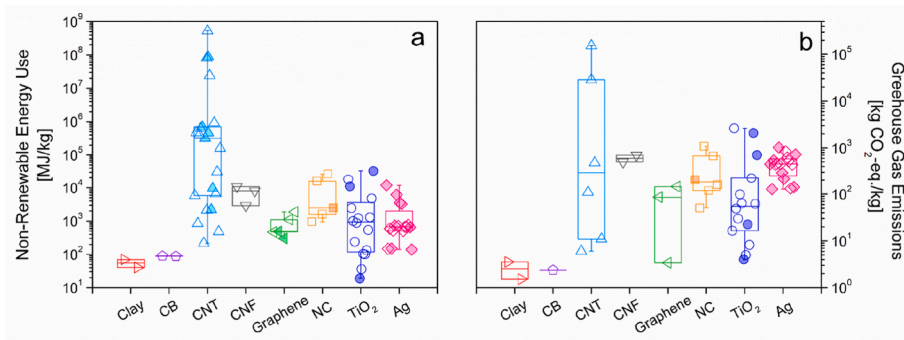


Fig. 2. Greenhouse gas emissions and non-renewable energy use of biopolymers (open symbols) and recycled plastics (full symbols). Red circles refer to commodity petroleum-based plastics (PP, PET, HDPE, LDPE) and are shown as reference. The turquoise box represents the region containing 75% of collected data for green plastics. The list of data, complete with bibliographic references, is provided in Appendix A, Table A1.



**Fig. 3.** Non-renewable energy use (a) and greenhouse gas emissions (b) for different kinds of nanoparticles. Full and empty symbols refer to nanoparticles synthesized with physical and chemical methods, respectively. The same data, complete with bibliographic references and more specific information on the synthesis procedure, are listed in [Appendix A, Table A2](#).

such an “exfoliation” to occur, the clay layers require surface modifications that make them more organophilic. This is usually done with exchange reactions, which link to the clay surface cationic surfactants such as quaternary alkylammonium salts (Liu, 2007). Joshi estimated that, from cradle to factory gate, the organic modifier accounts for 56.4% of energy use, 31% of global warming effects, and about 50% of the emissions of acidifying substances. Despite this relevant environmental burden, organic modification is essential to enhance clay dispersibility and to improve polymer-clay interactions. This can lead to PNCs with superior specific properties at low nanoparticle content, with obvious environmental benefits. Therefore, functionality-based LCA approaches are always recommended in case of organo-modified clays and, more in general, when surface-modified nanoparticles are used. Going back to the overall impact of organoclays, Joshi estimated an energy demand of 40.1 MJ per kg of filler, while the GWP was 1.520 kg of CO<sub>2</sub>-eq. kg<sup>-1</sup>. These data are of the same order of magnitude as those of conventional glass fibers, which instead perform better than organoclays in terms of water emission. It is important to note that the comparison is made at equal amount of filler, but since organoclays are typically added in much lower amounts (~1 wt% versus ~10 wt% for conventional fillers), the filler-related impact in PNCs should be lower. Roes et al., estimated NREU of 69.7 MJ and GWP of 3.55 kg of CO<sub>2</sub>-eq. for producing 1 kg of organoclays (Roes et al., 2010). The discrepancies with the estimates by Joshi were ascribed to the uncertainty in life cycle inventory data for clay production, largely based on personal communications from manufacturers. In any case, the authors consider negligible the impact of organoclay production because of the low amounts of filler employed in the PNCs (Roes et al., 2007a). As will be discussed in Section 4, such an assumption could be misleading.

### 3.2.2. Carbon-based nanoparticles

Carbon-based nanoparticles are widely used in rubber and plastic industry. The most common carbonaceous fillers are carbon black (CB), CNTs and, in last decade, graphite-derived nanoplatelets. CB is the generic name for paracrystalline nano-sized particles formed in the gas phase by the thermal decomposition of hydrocarbons. Despite its large employ (11.4 Mt consumed in 2013 (Spahr and Roth, 2016)), scarce information is available regarding the environmental impact of CB. Ecoinvent v2.2 database reports an embodied energy for CB production of 89 MJ kg<sup>-1</sup>, while an estimate of greenhouse gas emissions of 2.368 kg of CO<sub>2</sub>-eq. kg<sup>-1</sup> can be derived from (Lin et al., 2017).

CNTs are hollow, seamless, one-dimensional cylinders (diameter of order of 10<sup>1</sup> nm) deriving from the wrapping of one (single walled) or many (multi-walled) graphene layers. This kind of nanoparticles has received growing attention as nanofiller for PNCs because of superior mechanical strength and enhanced electrical and thermal conductivities. Regarding their environmental impact, several studies have discussed the energy requirements for CNT production and purification

(Kushnir and Sandén, 2008; Roes et al., 2010; Zhai et al., 2016) and the related greenhouse gas emissions (Healy et al., 2008; Kushnir and Sandén, 2008; Roes et al., 2010; Singh et al., 2008; Teah et al., 2020) and health effects (Buist et al., 2017; Köhler et al., 2008; Singh et al., 2008). A distinctive feature of this literature is the considerable discrepancy between environmental impact data, which reflects the variety of products (single- or multi-walled CNTs, differing in terms of degree of purity and structural quality), manufacturing processes (arc ablation, chemical vapor deposition (CVD), or high-pressure carbon monoxide), and process assumptions (production scale, reaction yield, reaction temperature). A nice review by Upadhyayula et al. summarizes the energies required to produce CNTs by different methods, precursors, catalysts, and product characteristics, reporting values that range between 4.8 10<sup>2</sup> MJ kg<sup>-1</sup> (CVD based on floating catalyst bed) and 8.7 10<sup>7</sup> MJ kg<sup>-1</sup> (laser ablation) (Upadhyayula et al., 2012). As much as discordant, it is undeniable that the energy burden for CNT production is very high when compared to other nanofillers. The same conclusion can be drawn for carbon nanofibers (CNFs), which differ from CNTs for diameter (order of 10<sup>2</sup> nm) and structure of the cylinders. The production of CNFs also requires high energies, ranging from 2.8 10<sup>3</sup> to 1.09 10<sup>4</sup> MJ kg<sup>-1</sup> depending on the feedstock (Khanna et al., 2008). The main reasons why CNTs and CNFs are so energy expensive are: (i) high cost for raw material acquisition and manufacturing process; (ii) depletion of non-renewable resources; (iii) typically low reaction yield (see Fig. 4).

Moreover, when intended for PNCs, a further contribution must be considered due to (iv) the functionalization step needed to favor nanoparticle dispersion in the host polymer. Two approach can be adopted for this purpose: (i) chemical functionalization, in which moieties are covalently bound to the CNT sidewall or tube tips; (ii) physical methods, based on the interactions between the active molecules and carbon atoms on the CNTs (Ma et al., 2010). Wu et al. recently compared the environmental impacts of these two functionalization strategies, concluding that the physical route is from 40 to 80% less impacting than the chemical one (Wu et al., 2020). Regarding greenhouse gas emissions, as for energy data, substantial discrepancies are found in literature depending on the production process and quality of the products. Teah et al. reported values ranging from 0.480 to 28.55 kg CO<sub>2</sub>-eq. per g of high-quality single-walled CNTs produced by CVD (Teah et al., 2020); much lower emissions (order of 10<sup>1</sup>–10<sup>2</sup> kg CO<sub>2</sub>-eq. per kg of CNTs) were instead estimated for standard CNTs produced at industrial scale, with possible further reductions in case of reuse or sale of the byproducts of the CNT synthesis (Roes et al., 2010; Singh et al., 2008). Khanna et al. reported GWP between ~500 and ~700 kg of CO<sub>2</sub>-eq. per kg of CNFs (Khanna et al., 2008). Overall, the fact remains that both the greenhouse gas emissions and, above all, the energies involved in the synthesis of CNTs and CNFs are high (see Fig. 3). Therefore, thorough LCA analyses are strongly recommended to assess whether the benefits of PNCs based on such kind of nanoparticles offset the heavy environmental burden

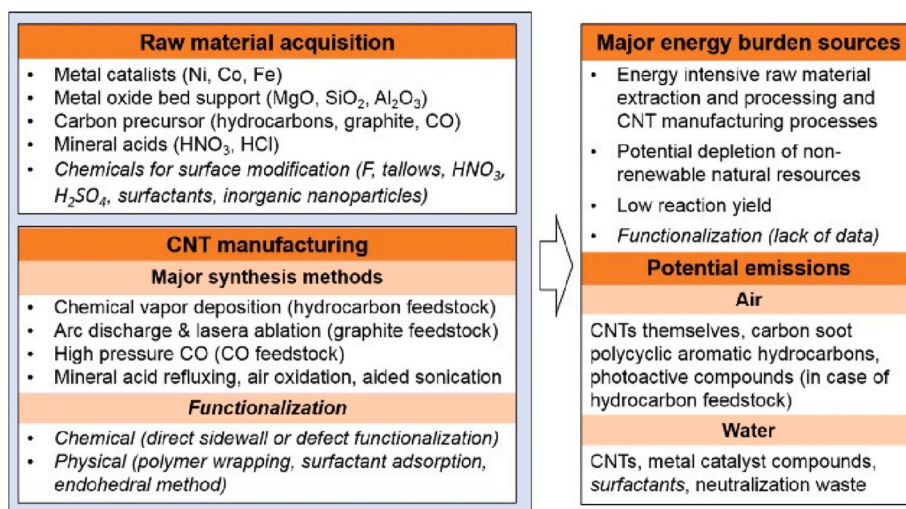


Fig. 4. CNT manufacturing and related energy burden sources and potential emissions. Readapted from (Upadhyayula et al., 2012) with copyright permission of Elsevier. The contributions related to CNT functionalization are added in italic.

related to their production.

The last class of carbon-based fillers considered in this subsection is graphene-like nanoparticles. Graphene is a single-layer carbon sheet with a hexagonal packed lattice structure. It is an excellent candidate for high-performance PNCs due to many unique properties, such as large theoretical specific surface area ( $>2500 \text{ m}^2 \text{ g}^{-1}$ ), high Young's modulus ( $\sim 1 \text{ TPa}$ ), and excellent thermal conductivity ( $3000 \div 5000 \text{ W m}^{-1} \text{ K}^{-1}$ ) (Huang et al., 2012). The methods for obtaining graphene-based nanoparticles can be divided in "bottom-up" (synthesis from a carbon source) and "top-down" approaches (exfoliation of bulk graphite). Here we only consider top-down approaches, whose high throughput and ease of implementation make them preferable for the synthesis of nanoparticles for PNCs. In particular, we restrict our analysis to nanoparticles produced by (i) sonication of graphite in solvents, (ii) thermal exfoliation of intercalated graphite, and (iii) reduction of highly oxidized graphene oxide (GO). The latter is usually obtained by the Hummers' method via the reaction of graphite with a mixture of potassium permanganate and concentrated sulfuric acid. The reduction step can be accomplished in many ways (chemical reduction, thermal reduction, sonolysis, microwave-assisted reduction). Papanicolaou et al. recently estimated the cradle-to-gate environmental impact of a commercial-grade water suspension at 5 wt% of graphite nanoplatelets in the framework of a wider study on the sustainability of graphene-reinforced concrete for self-sensing structures (Papanikolaou et al., 2019). The nanoparticles were produced by sonication of graphite in solvent. The authors reported a GWP of 0.17 kg of CO<sub>2</sub>-eq. per kg of suspension. Such a low value is likely related to the relatively low quality of the filler produced (14 nm-thick, 25  $\mu\text{m}$ -large). Cossutta et al. compared the impacts of different graphene production routes over different production scales (Cossutta et al., 2017). The authors found that chemical oxidation is the least impacting route to produce large quantities of graphene, and that this holds true at both laboratory and (simulated) commercial scale. The estimated GWP at the lab scale was 86/146 g CO<sub>2</sub>-eq. per gram of reduced GO (thermal/chemical reduction), the biggest contributions being those related to the use and neutralization of acids in the oxidation step. Regarding energy consumption, the chemical nature of the process implies negligible values of electricity ( $3 \div 5 \cdot 10^{-1} \text{ MJ}$  per gram of nanoparticles). A slightly higher value of  $1.1 \cdot 10^3 \text{ MJ kg}^{-1}$  was reported in (Arvidsson et al., 2014), where the main contribution was ascribed to the chemical reduction process due to heating and high energy use for the production of the reducing agent (hydrazine). In the same study, lower energy consumption resulted for graphene obtained by ultrasonication in diethyl ether ( $4.7 \cdot 10^2 \text{ MJ kg}^{-1}$ ). Pizza et al. estimated 1.88

$10^3 \text{ MJ kg}^{-1}$  for graphene produced by thermal expansion of a sulphate-graphite intercalated compound (Pizza et al., 2014).

### 3.2.3. Cellulosic nanoparticles

Nano-structured cellulose, also referred to as nanocellulose (NC), is extracted from cellulose by pre-treatment of natural resources (mainly wood and plants) followed by acid treatment (cellulose nanocrystals) or mechanical disintegration (cellulose nanofibers). Due to low cost, low density ( $\sim 1.6 \text{ g cm}^{-3}$ ), biodegradability and high mechanical properties (stiffness  $>200 \text{ GPa}$ , tensile strength  $\sim 10 \text{ GPa}$ ), NC is receiving growing attention as nanofiller for PNCs (Dufresne, 2012; Kargarzadeh et al., 2017). Despite its natural origin, the environmental burden of NC is far from being low. Besides the investments to grow plants, from water to fertilizers, the pre-treatment of lignocellulosic biomass and the subsequent NC extraction is typically expensive. First, the lignocellulosic biomass needs bleaching (sodium chlorite, and acetic acid at  $70\text{--}80 \text{ }^\circ\text{C}$ ) or alkaline pre-treatment (sodium hydroxide). Then, if the chemical route is pursued, the delignified fibrils are subjected to acid hydrolysis, generally with sulfuric acid; if mechanical treatments are instead considered, intensive shear stresses are applied to the fibrils by means of high pressure homogenization, ultrasonication, or ball milling methods (Phanthong et al., 2018). Further burdening of the environmental impact derives from the chemical surface treatments performed to mitigate some of the NC drawbacks, such as high moisture absorption, poor wettability, and incompatibility with most polymeric matrices. The impact of different extraction methods has been the subject of several LCA studies on NC. Among others, Li et al. compared four lab scale NC fabrication routes involving chemical pre-treatment (2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation or chloroacetic acid etherification) and mechanical disintegration (sonication or homogenization) (Li et al., 2013). The cumulative energy demand varied between 34.7 and 176.1 MJ per 10 g of NC, being dominated by the large environmental footprint relative to raw material extraction process. The GWP ranged between 1.9 and 11.6 kg CO<sub>2</sub>-eq. (basis: 10 g of NC). A similar comparative analysis was performed by Arvidsson et al., who reported lower values of the cumulative energy demand (from  $\sim 100$  to  $\sim 1800 \text{ MJ kg}^{-1}$ ) and GWP values (from  $\sim 1$  to  $\sim 100 \text{ kg CO}_2\text{-eq. kg}^{-1}$ ) (Arvidsson et al., 2015). Brito de Figueirêdo et al. focused on the source of the NC, comparing the impacts of cellulose nanowhiskers produced from acid hydrolysis of unripe coconut and cotton fibers (De Figueirêdo et al., 2012). The former brought about higher impact due to lower cellulose content and yield of the extraction process. More recently, the same research group addressed the environmental impact of different

methods for the extraction of cellulose nanocrystals from coconut fibers, concluding that high-power ultrasonication should be preferred compared to acid treatments (Nascimento et al., 2016). Koch et al. considered the environmental implications of a prototypical biorefinery for the production of lignin nanoparticles from wheat straw (Koch et al., 2020). The cradle-to-gate investigation focused, among other impact categories, on GWP, reporting values between 80 and 240 kg of CO<sub>2</sub>-eq. per kg of nanoparticles depending on the setup of the precipitation and purification process steps. A credit of 40 kg of CO<sub>2</sub>-eq. kg<sup>-1</sup> was considered because of the fixation of CO<sub>2</sub> from wheat straw cultivation, and the optimal plant setup was found to depend on a balance between the number of membrane units considered for solvent recovery (ethanol), and the extra-energy demand for the additional filtration steps. Solvent and thermal energy were found to be the hotspots of the process, accounting for 80–99% of the GWP.

### 3.2.4. TiO<sub>2</sub> nanoparticles

TiO<sub>2</sub> is a white crystalline-type wide bandgap semiconductor that finds its main application in paints, varnishes, paper and plastics, but it is also widely used in food, cosmetics, medicine, catalysis, and many other areas (Mueller and Nowack, 2008). As filler for polymer matrices, TiO<sub>2</sub> nanoparticles are used to produce PNCs with enhanced mechanical, dielectric, biocide, and thermal properties (Bet-Moushoul et al., 2016; Fu et al., 2005; Ghosh and Das, 2015; Acierno et al., 2007). The environmental impact of TiO<sub>2</sub> nanoparticle production significantly vary as a function of the synthesis method, which in turn affects nanostructure and inclination to agglomeration of the particles. Osterwalder et al. compared wet-chemistry and dry processes, concluding that the latter imply much higher energy consumptions (Osterwalder et al., 2006). A systematic analysis of several routes covering physical, chemical, and biological synthesis was recently performed by Wu et al. (2019). Chemical routes need less energy and generate less greenhouse gas emissions than physical and biological ones. Physical methods, however, are more versatile and easier to apply in industrial mass production. This is an important point: preferring a method over another should be not only a matter of environmental impact, but practical aspects must be considered as well. Such a critical approach can be found in (Stieberova et al., 2019), where a comparison matrix is provided in

which various synthesis methods are compared in terms of production rate, quality, cost of equipment, and variability of each technique (Fig. 5).

Regarding the impact of TiO<sub>2</sub> nanoparticles, the authors proposed a continuous-flow hydrothermal synthesis that requires non-renewable energy of 239.7 MJ kg<sup>-1</sup> and emits 16.52 kg CO<sub>2</sub>-eq. kg<sup>-1</sup>. Other NREU and GWP data, either collected from cradle-to-gate studies (Grubb and Bakshi, 2011; Manda et al., 2012; Pini et al., 2015) or extrapolated from cradle-to-grave analyses (Tichá et al., 2016; Zhang et al., 2017), are summarized in Appendix A, Table A2. On average, the production of TiO<sub>2</sub> nanoparticles is slightly less impacting than that of other nanoparticles (see Fig. 3). This could reflect the technology readiness level of the production methods of this type of nanoparticles, which have been used for a long time in many industrial sectors.

### 3.2.5. Ag nanoparticles

Due to superior physical, chemical, and biological characteristics, Ag nanoparticles are largely employed in many industrial fields (Natsuki, 2015; Temizel-Sekeryan and Hicks, 2020). Prevalent applications are in medical/cosmetics sectors, which benefit from the inherent antibacterial properties and low toxicity of this class of nanoparticles, and in the electronic industry, in which conductive inks containing Ag nanoparticles are often used in the production of electronic boards. As far as PNCs are concerned, the antibacterial features of Ag nanoparticles are mainly exploited in textiles and packaging. The production step of Ag nanoparticles is the main responsible for the overall environmental impact of Ag-based PNCs. Pourzahedi & Eckelman estimated that impacts associated with the upstream production of bulk silver contribute to over 90% of life cycle burdens (Pourzahedi and Eckelman, 2015). Regarding the comparison among various processes, flame spray pyrolysis was found to be the most impacting Ag production method because of low yields and intensive electricity use. Physical processes resulted more impacting than chemical ones also in (Temizel-Sekeryan and Hicks, 2020). Things might change when, rather than on a mass basis, the comparison is made on a functional basis. For example, Pourzahedi & Eckelman observed that physical syntheses can lead to very small nanoparticles with high antimicrobial efficacy, making this kind of processes preferable over chemical ones (Pourzahedi and

Technology/ Criterion	Production rate	Quality	Variability	Cost of inputs	Cost of equipment	Energy Consumption process	Energy Consumption embodied	CO <sub>2</sub> emissions
CFHS	High	Very good	Very high	Different	Medium	Low	Different	Low
VAFS	Very high	Good	Low	Low	Very High	Low	Low	Low
Sulfate process	High	Good	Low	Low	High	Low	Low	Low
Altair	High	Good	Medium	Low	Medium	Low	Low	Low
HT plasma	High/medium	Good	High	Different	Medium	Very high	Different	High
FSP	Medium	Good	High	High	Medium	Low	High	Medium
LT plasma	Low	Very good	Medium	Different	Medium	N/A	Different	N/A
CS solution	Low	Very good	High	High	Low	N/A	High	N/A
Sol-gel	Low	Very good	Very high	Different	Low	High	Different	High
Solvothermal	Low	Very good	Very high	High	Medium	N/A	High	N/A
Hydrothermal	Low	Very good	Very high	High	Medium	N/A	High	N/A
Precipitation	Low	Very good	Very high	Different	Low	High	High	High

Fig. 5. Comparative matrix to compare different technologies for nanoparticle production. Abbreviations: continuous-flow hydrothermal synthesis (CFHS), vaporized aerosol flame synthesis (VAFS), high- (HT) and low-temperature (LT) plasma, flame spray pyrolysis (FSP), combustion solution synthesis (CS). Image readapted from (Stieberova et al., 2019) with copyright permission of Elsevier.



Eckelman, 2015). Regarding the absolute values of environmental burdens, the production of Ag nanoparticles requires relatively low NREU values, ranging between  $\sim 10^2$  and  $\sim 10^4$  MJ kg<sup>-1</sup>, but the GWPs are quite high, reaching hundreds of kg CO<sub>2</sub>-eq. per kg of nanoparticles. To compensate this burden, Zhang et al. proposed to combine Ag with other lower impact nanoparticles such as TiO<sub>2</sub> (Zhang et al., 2017). It is worth noting that the relationship between the amount of nanoparticles and their impact can be not trivial. Comparing the percentage impact of Ag nanoparticles for a series of products, Pourzahedi et al. found a good correlation between nanoparticle content and percentage impact for GWP and fossil fuel depletion, while less clear trends emerged when looking at other impact categories (Pourzahedi et al., 2017). In particular, the percentage of released nanoparticles does not increase proportionally with their initial content, so the same happens with human health-related risks due to nanoparticle release.

### 3.2.6. Other nanoparticles

The majority of PNCs we are interested in are based on the nanoparticles discussed in previous sections. However, many other nanoparticles can find applications in a variety of technical applications and consumer products, leading to a continuous increase in production, manufacture and use of materials containing “engineered nanomaterial” (Gottschalk and Nowack, 2011). Among others, nano-sized ZnO, ZrO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub>, Au, LiFePO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, are sometimes used as filler to provide reinforcement or, more often, functionalities absent in a host polymer matrix (e.g. antibacterial activity, electrical conductivity, dielectric strength, magnetic features). To complete our collection, data of energy consumption and greenhouse gas emissions are provided for such nanoparticles in Appendix A, Table A2. Overall, the impacts are high because of their energy-intensive synthesis procedures, which sometimes need additional processes to reduce particle size down to the nanometer scale.

## 4. Contributions of green matrices and nanoparticles to the PNC production phase

The environmental impact of multicomponent materials such as PNCs is the weighted sum of the contribution of its components over each life phase, namely polymer and nanoparticle production, PNC manufacturing, transport, use, end of life. Here we limit our analysis to the first two stages, which lead to PNC granules ready to be further processed out of the PNC factory gate.

### 4.1. Polymers and nanoparticles production

The data collected in Section 3 can be exploited to help researchers and manufacturers in a conscious selection of polymers and nanoparticles for producing PNCs with low environmental impact.

Called  $x$  the mass fraction of nanoparticles, once the impact of nanoparticles ( $I_{NP}$ ) and polymer ( $I_p$ ) are known, the impact of the PNC is given by  $I_{PNC} = x I_{NP} + (1-x) I_p$ . Using this simple additivity rule, an approximated estimate of the impact of a generic PNC in terms of raw materials can be obtained. Fig. 6 shows the result of such a procedure for the categories  $I =$  NREU and GWP. Since the data of green polymers are gathered in a quite dense cloud (see Fig. 2), common values of NREU = 47.3 MJ kg<sup>-1</sup> and GWP = 1.59 kg CO<sub>2</sub>-eq. kg<sup>-1</sup> were assumed for the polymer matrix of our hypothetical PNCs. These data represent the average values of all NREU and GWP data collected in Appendix A, Table A1. Regarding the nanoparticles, distinct average values were used for each class of filler. To compute the  $I_{PNC}$  values, the mass fraction of nanoparticles is needed. The value of  $x$  can significantly differ depending on type of nanoparticle and final application of the PNC. A reasonable reference value for typical filler loadings is represented by the percolation threshold,  $x_p$ , i.e. the amount of filler required for a continuous nanoparticle network to build up throughout the host matrix. Once this happens, many mechanical and functional properties of

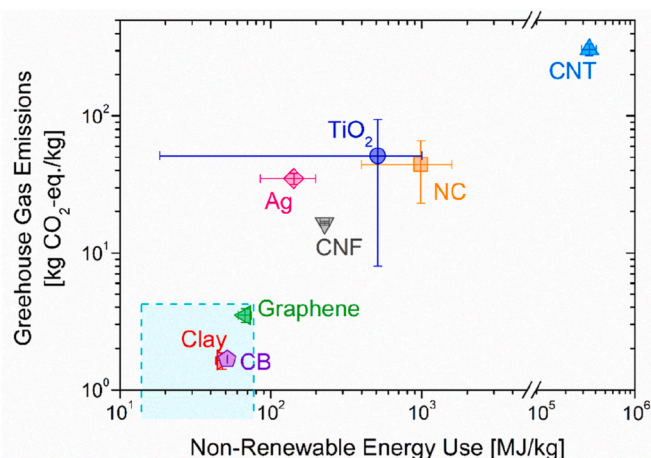


Fig. 6. Estimated values of greenhouse gas emissions and non-renewable energy use for the material production phase of typical green PNCs. The data were computed through the additivity rule by assuming typical amounts of nanoparticles (Appendix A, Table A3). For each class of nanoparticles, average values of the GHG emissions and NREU data reported in Fig. 3 were considered; common values of GHG emissions (47.6 Kg CO<sub>2</sub>-eq. kg<sup>-1</sup>) and NREU (1.64 MJ kg<sup>-1</sup>) were instead assumed for the green matrices. Error bars reflect the variability of the data of nanoparticles of Fig. 3. The turquoise box represents the zone in which 75% of the green polymer matrices fall (limitedly to positive GWP and NREU data; same as shown in Fig. 2).

PNCs begin increasing, hence the filler percolation is often sought by researchers and manufacturers. Typical values of  $x$ , either based on  $x_p$  or inferred from a review of the literature, are reported in Appendix A, Table A3 for each class of nanoparticle. Based on these data, the plot showed in Fig. 6 was obtained. The region of the plot where 75% of unfilled green matrices fall is also reported as reference (turquoise box). The error bars reflect the variability of the data on nanoparticles.

This way of plotting data is a useful exercise for highlighting some interesting points. It clearly emerges that nanoparticles can substantially increase the environmental impact of the material production phase of PNCs by orders of magnitude. The effect, however, strongly depends on the type of nanoparticles, which can be roughly divided into three groups:

- (i) Clay, CB and graphene, whose presence does not appreciably alter the impact of the PNC respect to that of the unfilled matrix;
- (ii) Ag, CNFs, TiO<sub>2</sub> and NC, which make the PNC about ten times more impacting than the host matrix;
- (iii) CNTs, which have a huge impact and cause increases of GWP and NREU of  $\sim 2$  and  $\sim 4$  orders of magnitude compared to the polymer matrix.

The presence of graphene in the group of the least impacting nanoparticles is noteworthy. This could reflect the huge interest in this new class of nanoparticles, which brought to highly optimized synthesis procedures. However, further studies are highly desirable to corroborate this conclusion. Less surprising is the datum on nano-clays and CB, which are widely used nanoparticles with well-established synthesis procedures. In contrast, the use of CNT-based PNCs is very impacting, especially in terms of energy demand. The use of this class of PNCs could be questionable for large-scale applications (e.g., in packaging, automotive and transport sectors), while advantages could be possible for high added-value products, i.e. in which the technological benefits outweigh environmental aspects. Regarding the intermediate group of nanoparticles (Ag, CNFs, TiO<sub>2</sub> and NC), the ten-fold increase of both NREU and GWP is a heavy burden, and a careful functionality-based LCA analysis is required to assess whether a PNC is really sustainable. This is

a general rule when dealing with PNCs, whose environmental sustainability strongly depends on their final performances. In this regard, the analysis of the literature suggests not to disdain apparently counterintuitive approaches, such as (i) increasing the amount of filler (see Fig. 1) or (ii) functionalizing the nanoparticles to promote their fine and uniform dispersion within the host matrix. Achieving this goal is particularly difficult, hence functionalization is crucial, in case of high aspect ratio nanoparticles such as CNTs, which tend to entangle forming tight bundles (Salzano de Luna et al., 2013), or with layered nanoparticles such as clays and graphene (Sham and Notley, 2013; Ting et al., 2019), which are generally difficult to be exfoliated. Besides promoting dispersion, functionalization hinders reaggregation phenomena during melt compounding and enhances the quality of nanoparticle-matrix interface, with further beneficial effects in terms of final performances.

#### 4.2. Manufacturing phase

Obtaining a well-dispersed PNC means forcing the host polymer matrix to break/loose the filler aggregates, possibly isolating the single nanoparticles. Dealing with high viscosity matrices is advantageous for this purpose because of the high viscous stresses transmitted to the filler during mixing. This is the case of thermoplastics polymers, for which melt compounding methods are largely employed. The main mixing apparatus for dispersing fillers in polymer matrices for large-scale production is the extruder. The energy required to melt the polymer granules, mix them with the desired amount of nanoparticles, and pelletize the extrudate for obtaining PNC granules ready to be processed is  $\sim 1.64$  MJ kg<sup>-1</sup> and is mostly by electricity (Vlachopoulos, 2009). Assuming greenhouse gas emissions of  $\sim 0.4$  kg CO<sub>2</sub>-eq. per kWh (Williams et al., 2012), the manufacturing phase would emit 0.19 kg CO<sub>2</sub>-eq. per kg of PNC. Both energy consumption and GHG emissions of the manufacturing phase are, hence, negligible if compared to that of the material production phase (see Fig. 6). Things could change if alternative nanoparticle dispersion methods are considered. Among others, additive manufacturing (AM) techniques by fused deposition modelling have been recently proposed as an alternative to traditional melt compounding techniques. Many hindrances remain in the production of PNCs by AM because of inadequate dispersion of the filler, nanoparticle alignment in the printing direction, printability issues due to the peculiar rheological behavior of nanofilled polymers, relatively low production rates (<50 kg/h), high costs for large scale production (Al Rashid et al., 2021). As a result, a lack of LCA studies on the impact of AM exists in the literature, and the possible advantages of resorting to such new manufacturing techniques, if any, remain to be assessed. Solvent-based methods (e.g.: solution mixing) have been often pursued in past, but they require the use of large amounts of solvents, whose impact is due to their inherent environmental burden as well as to the energy required to remove the solvent after mixing. Energy intensive processes (e.g.: sonication) can be also necessary to favor nanoparticle dispersion. This is also the case of PNCs based on thermosets, whose manufacturing starts with the dispersion of the filler in a low-viscosity uncured resin (Koerner et al., 2006). Even in such cases, however, the impact of raw materials is expected to be the most impacting phase of PNC production. Therefore, a conscious section of matrices and (above all) nanoparticles is the most crucial step towards the production of low-environmental impact PNCs.

#### 5. Conclusions

The environmental sustainability of green PNCs is a complex matter that depends on many interrelated factors. From an environmental point of view, biobased/biodegradable polymers and recycled plastics are only marginally preferable with respect to their petroleum-based counterparts. As a result, the environmental advantage of using PNCs mostly depends on the nanoparticles. Significant variability has been found in the literature for NREU and GWP data of nanoparticles.

Differences exist not only among different types of filler, but also within the same family of nanoparticles because of the many possible synthesis routes. Overall, both greenhouse gas emissions and energies involved in the synthesis of nanoparticles are much higher than those of the green matrices. As a result, even if added in very low amounts, nanoparticles can compromise the overall sustainability of green PNCs. The key is assessing whether the benefits of using nanoparticles offset their environmental burden. This can be done adopting functionality-based LCA approaches, in which analyses and comparisons are made at equal performance. Achieving excellent properties is, hence, crucial to ensure the sustainability of a PNCs. High performances can lead to material saving and, in case of substitution of heavier materials such as metals, to environmental benefits during the lifecycle of the products (especially the transport and use phases). Seeking for high performances can lead to counterintuitive results. For example, PNCs can result more sustainable if high content of nanoparticles are used. Moreover, functionalized nanoparticles can be preferable with respect to their unmodified counterparts despite the environmental burden of the functionalization step. Aiming at drawing general conclusions to produce truly sustainable green nanocomposites, the impact of typical PNCs based on different classes of nanoparticles has been estimated. Nanoparticles can be roughly divided into three groups: (i) organoclay, carbon black and graphene-like nanoparticles, which do not alter the environmental impact of the host polymer matrix; (ii) carbon nanofibers, nanocellulose and TiO<sub>2</sub> and Ag nanoparticles, which cause a ten-fold increase of both NREU and GWP compared to the unfilled matrix; (iii) CNTs, which are extremely impacting, especially in terms of NREU. Although such conclusions suffer from the strong simplifying assumptions made to rationalize the data, useful information is provided for an informed selection of materials and processes for producing truly sustainable green PNCs.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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