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Release and toxicity assessment of carbon nanomaterial reinforced polymers during the use and end-of-life phases: A comparative review

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ABSTRACT

The research on carbon-based nanomaterial (C-NM) composites has increased in the last two decades. This family of functional materials shows outstanding mechanical, thermal and electrical properties, and are being used in a variety of applications. An important challenge remains before C-NM can be fully integrated in our production industries and our lives: to assess the release of debris during production, use, and misuse of composites and the effect they may have on the environment and on human health. During their lifecycle, composites materials can be subjected to a variety of stresses which may release particles from the macroscopic range to the nanoscale. In this review, the release of debris due to abrasion, weathering and combustion as well as their toxicity is evaluated for the three most used C-NM: Carbon Black, Carbon Nanotubes and Graphene-related materials. The goal is to stimulate a Safe-By-Design approach by guiding the selection of carbon nano-fillers for specific applications based of safety and performance.

1. Introduction

Composite materials are a relatively young family of functional materials. The first fully synthetic polymer plastic, the thermoset Bakelite, was created by Belgian chemist Leo Baekeland in 1907 (Streit-Bianchi et al., 2020). In the 1930s, today's major thermoplastics materials such as polystyrene (PS), Poly(vinyl chloride)(PVC), the polyolefins family, and polyester resins began to be produced industrially (Gilbert et al., 2017). This class of materials exhibits attractive properties such as low density and a simple processability but show mediocre mechanical properties compared to their metallic counterparts (MacDiarmid, 2001; Rösler et al., 2007). Nevertheless, they offer the ideal matrix to host a variety of reinforcement fillers to enhance mechanical, thermal, and electric characteristics of the polymers (Ramasubramaniam et al., 2003). The birth of Fibre Reinforced Plastics (FRP) occurred in the late 1935–40 when Owens Corning produced the first fibre composite boat and Henry Ford used glass fibres (GF) composite materials in the automobile industry (Bhatt et al., 2018). Since then, an incredible diversity of composite materials has been designed for a wide range of applications, using different matrices and fillers from the macro to the nanoscale. A recent review from Tschiche et al. (2022) and several studies (Singh et al., 2019; Singh et al., 2022; Watson-Wright et al., 2017) explored the potential of nanomaterials in different product groups, highlighting their applications but also tackling the toxicological challenges that the nanomaterials represent for human health. The work of Arvidsson et al. (2022), as well as the French R-nano (de la transition ecologique, 1999), collecting the mandatory declaration of substances since 2022, give a glimpse into the future, using available production volume data to forecast the increase in the use of nanomaterials in functional materials and assessing the environmental risks of their release in aquatic environments. These publications show the potential of nanomaterials in today's world, but call for further research in the most important aspect of any innovation: safety for health and environment.

In this review, we consider a family of nanomaterials, namely Carbonaceous Nanomaterials (C-NM), as high performance nano-fillers in polymers, focusing on the release from the polymer matrix during the life cycle of the composite and the possible impacts on human health of such debris.

C-NM are a class of nanomaterials (NMs) based on carbon, such as fullerenes, carbon nanotubes (C-NT), graphene and its derivatives, graphene oxide, nanodiamonds and carbon based quantum dots (Patel et al., 2019). Because of their light weight and outstanding mechanical, electrical and thermal properties C-NMs have emerged as a novel

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candidate for next generation high performance composite fillers (Yaragalla et al., 2019), competing with the existing carbon fibres (CF) and in large quantities produced GF. Despite the numerous advantages, the use of C-NM in composites also brings risk factors (Hurt et al., 2006; Chen and Wang, 2016; Parwez and Budihal, 2020; Luanpitpong et al., 2016; Singh et al., 2016). It is important to evaluate the potential release of nano-fillers from the composite during production, use or misuse and the end of life. The application for high performance composite materials ranges from civil infrastructure, aerospace, automobiles and military applications to textiles and biomedical applications (Kaur et al., 2015; Peters, 2013) Depending on the application, composite materials can be exposed to mechanical stresses, chemical processes, ageing, temperature and humidity changes, exposure to UV, combustion, abrasion and fatigue (Karbhari and Zhao, 2000; Karbhari, 2007; Malvar et al., 2007). This variety of stimuli, both in their nature and in their intensity, and their effect on the composite matrix and filler has to be understood to evaluate the magnitude of nanoparticles release. After the release is assessed, the fate of the particles, their potential toxicity and their stability has to be determined to prevent accumulation and damage in the human body and in the environment. Although their properties are very attractive, the safety of novel C-NM composites should remain a priority for producers and researches alike.

Moreover, this knowledge is extremely relevant to apply a Safer-by-Design (SbD) approach, as it could guide the selection of nano-fillers based on the intersection of improved performance, specific application, and use phase and end of life risk.

The SbD approach aims at integrating considerations about the product safety early during the R&D process, in this way pruning out in an early development phase all those design options that would pose a risk to humans and the environment (Schmutz et al., 2020; Patinha Caldeira et al., 2022). To achieve this goal, it is important to understand the link between the use of different NMs, the exposure and hazard risks of the nano-containing product, ideally relating such differences to the properties of the NM/polymer system (Kraegeloh et al., 2018).

To support a SbD application of C-NM in reinforced composites, in this review we investigated and explored the relationship between the C-NM, the polymer matrix, and how they affect the release and toxicity of particles during the use and end-of-life phases compared to the matrix alone. By combining together the information on release and toxicity, we provide a first qualitative assessment of the potential risks and data gaps for the use and end-of-life phases of C-NM reinforced composites (see Fig. 1).

2. Application of C-NM in composites

C-NM are a class of filler in polymers which show excellent mechanical, thermal and electrical properties. The first carbon based filler was used in 1970 when DuPont developed an aramid fibre known as Kevlar and specialized composite materials increased their potential in fields which required cutting edge mechanical properties (Nagavally, 2017). CF began to be employed as an improvement to GF, providing enhanced mechanical properties at the detriment of an increased production cost. Unlike other carbon nanomaterials, Carbon Black (CB) has been used since the ancient times. Due to being a residue of incomplete combustion (Fu et al., 2016), it can be found as a pigment in wall paintings in Paleolithic caves.

In this section the three main families of C-NMs, Carbon Black(CB), Carbon Nanotubes (C-NT) and graphene related materials, employed as fillers in composites are presented. Today, the production volumes of CNT and GRM are smaller compared to CB or GF, and could be considered as niche products, due also to their production costs. However, in high-value and high-end applications such as aerospace and sporting goods the advanced properties of CNT and GRM provide a clear advantage compared to CB and GF, given for example the lower amount of filler needed to reach the same electrical conductivity, or the lighter weight and higher strength and resistance (Sun et al., 2013).

2.1. Carbon black

Carbon Black (CB) is a generic term for the most common amorphous carbon nanomaterial used to this day. There exist over 42 grades of CB, depending on the application, with varying aggregate size and distribution, morphology and surface activity (Wang et al., 2000). The most common applications for CB are as pigment in inks and as components in engineered plastics. In the second case, CB provides UV stab and reduces water uptake at low percentages, and increases the stiffness and conductivity of the plastic at high percentages. While its use started already in the early 1900's (Long et al., 2013), in 2001 the world capacity has been estimated at over 8 million metric tons (Wang et al., 2000).

Carbon Black is the most used form of CNM in composites. It is moslty used as a filler in elastomers, especially the tire industry, where it enhances tear resistance and improves the wear charactreristics of the tires (Donnet, 1993). CB has been reported to enhance properties such as UV protection, electrical conductance, opacity, change the fracture behaviour and improve abrasion and failure properties in both termoplastic and thermosets materials (Donnet, 1993; Buxbaum, 2008). Because of its electrical and thermal properties, there are examples of CB as a filler in an epoxy matrix for electrical heater applications (El-Tantawy et al., 2002). More recently, CB has been investigated as a flame retardant agent in polypropilene (PP) (Wen et al., 2012) and linear low density polyethilene (LLDPE) (Gong et al., 2014), resulting in significantly enhanced thermal stability.

2.2. Carbon nanotubes

Although the first Carbon Nanotubes (CNT), hexagonal organized carbon sheets enrolled as single or multi-walled tubes up to several 100 μm long fibres, were probably observed in the 1950's (O'connell, 2018), they were first fully characterized and named by Ijima in 1991 (Yang et al., 2008; Iijima, 1991). In the world of composites, CNT, similarly to other carbon-based reinforcement and filler materials, offer outstanding mechanical properties combined with low density, which results in light

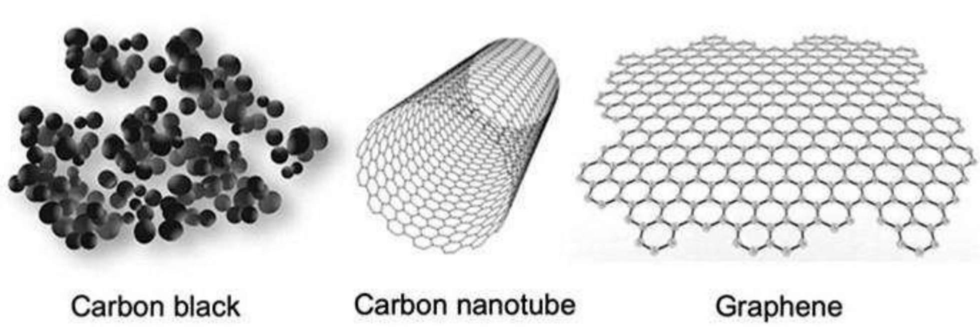

Fig. 1. A schematic not-to-scale representation of Carbon Black, Carbon nanotubes and graphene. Reprinted with permission from Tianyong et al. (2021).

and highly performing combinations. Furthermore, CNT are reported to exhibit excellent thermal and electrical conductive properties, remaining stable up to 2800 °C, boasting a thermal conductivity twice as high as diamond and an electric current carrying capacity 1000 times greater than copper (Thostenson et al., 2001; Endo et al., 2006). CNT and GRM, as standard carbon or glass fibres, can be processed through conventional polymer flow equipment which moulds the composite into complex shapes (Calvert, 1999). Epoxy resins have been shown to have increased strength when mixed with CNT to form composites (Breuer and Sundararaj, 2004; Tiano et al., 2000). The group of Kearns and Shambaugh (2002) increased tensile stress of polypropylene (PP) by adding 1% (by weight) of CNT. A similar study on polystyrene (PS) found a 40% increase in tensile strength and a twofold increase in Young modulus compared to PS alone upon addition of 2.49% (by volume) of CNT (Safadi et al., 2002). Electrical and thermal properties are also shown to be enhanced by CNT in several polymer matrix, such as PP, PS, polycarbonate (PC) and polymethil methacrylate (PMMA) (Breuer and Sundararaj, 2004; Lozano and Barrera, 2001; Gordeyev et al., 2000; Pötschke et al., 2002; Safadi et al., 2002).

CNT are also used in non-polymer-based composites. There have been a few studies regarding ceramic-based composites (Harris, 2004) and CNT in concrete (Wohlleben et al., 2011). Notably, Zhan et al. (2003) reports a threefold increase in fracture toughness in a CNT-Al_2O_3 ceramic composite compared to pure nanocrystalline alumina, while Sakamoto and Dunn (2001) used a Vanadium oxide-CNT composite to produce electrodes for use in Lithium batteries. Also in the field of metals CNT have been used to attempt to combine mechanical strength with a lower density, making these composites particularly interesting for the aerospace industry (Harris, 2004; Kuzumaki et al., 2000; Chen et al., 2003). In the medical field, Carbon Nanotubes have been added to lower the sintering temperature of metallic implants and add a composite bioactive layer (Kaya et al., 2008).

As a relatively new filler material, there are still difficulties to be addressed for CNT-composites. The CNT-matrix interface is a critical zone, where local failure can lead to drastic reduction in performance and overall composite failure (O'connell, 2018; Yang et al., 2008). Furthermore, agglomeration of the CNT and their production cost are a challenge for producers worldwide (Endo et al., 2006). Nevertheless, CNT show a great potential in the field of high performance composites for a wide range of applications.

2.3. Graphene-related materials

The first report of the preparation and isolation of single layers of graphene was reported in 2004 in Manchester (Young et al., 2012; Novoselov et al., 2004). A widespread interest from the scientific community has sparked significant advances in the characterization of graphene's electrical, mechanical and thermal properties and their potential applications. 2D nanosheets of graphene are reported to have the highest ever measured tensile strength (130 GPa) and Young modulus (1 TPa), a high specific surface area at 2360 m^2g^{-1} and best known thermal (5000$Wm^{-1}K^{-1}$) and electrical conductivity 10^8Sm^{-1}) (Zeinedini et al., 2018; Zhu et al., 2010; Young et al., 2012). Because of these Properties 2D graphene may arguably be the best candidate for high-performance carbon-based nanocomposites (Yu et al., 2017; Sun et al., 2021). Graphene related materials also offer a lower production cost and present less overall toxicological effects than CNT (Fadeel et al., 2018).

Graphene sheets as a filler in a polymer matrix can significantly enhance the mechanical properties of polymer matrices. For example, graphene increases fracture toughness by prolonging the crack propagation path in nanocomposites (Sun et al., 2021). The mechanical properties of the composite are however influenced not only by the presence of the NM, but also by the NM physico-chemical properties. In the case of a graphene-epoxy nanocomposite, Kim et al. (2017) found that the tensile strength and toughness increased by 77.6% and 215% when using respectively large-sized graphene (1 μm) and small-sized graphene (20 nm) (Kim et al., 2017). On the other hand, Graphene oxide (GO) composites do not always show a significant increase in mechanical properties compared the host polymer matrix (Young et al., 2012; Chen et al., 2008; Potts et al., 2011). This variance in properties within the graphene related nanomaterials highlights the need for improvement and optimization of carbon nanocomposites for mechanical applications. A small difference in filler material can lead to drastically different impacts on to the final composite which shows the importance of precise characterization of the filler carbon material by industrial producers.

Similarly to CNT, exfoliated carbon sheets from graphene oxide (GO) also provide percolated pathways for electron movement, enhancing the electrical conductivity of the resulting composite (Kim et al., 2010; Steurer et al., 2009). This has been shown using several different polymer matrices, such as polyolefins (Steurer et al., 2009), polyesters (Kim and Macosko, 2009; Kim and Macosko, 2008), acrylic and vinyl polymers (Liu et al., 2008; Liu et al., 2000; Wei et al., 2009; Jang et al., 2009), polyamide (Steurer et al., 2009), polyurethane (Kim et al., 2010; Raghu et al., 2008; Nguyen et al., 2009), and epoxy resin (Liang et al., 2009). Applications for these composite materials are antistatic coatings, conductive paints and electromagnetic shielding.

Graphene nanomaterials also have excellent potential in the field of high thermal performance composites (Halloran, 2006; Luo and Lloyd, 2012). A model simulation from Shen et al. (2016) shows that graphene sheets may greatly enhance the thermal conductivity in carbon-epoxy nanocomposites, reaching up to a 244% increase depending on the size, orientation, number of layers and distribution of the sheets in the polymer matrix. These results are in good agreement with the work of Balandin et al., which studied the properties of graphene/epoxy composites with few-layers graphene fillers.

Much like for CNT, the dispersion of graphene into the matrix and the interfacial stress, heat and electrical transfer are key challenges to successfully produce functional carbon nanocomposites (Gong et al., 2010; Legge et al., 2020). Although research and optimisation are still needed for graphene related materials as fillers for mechanical properties, they show significantly improved electrical and thermal characteristic compared with traditional composite materials.

3. Release from mechanical, thermal, and chemical stressors

Mechanical, chemical, and thermal stressors can cause the fragmentation/degradation of composites and the release of particles to the environment, from where they can then come in contact with humans and other living organisms (Froggett et al., 2014). Abrasion is a mechanical process that can happen during the manufacturing of products made of composite material, e.g. during cutting and drilling, as well as during the use phase, e.g. the abrasion of rubber tyres, or at the end of life, e.g. when products are ground to be reduced in smaller pieces before treatment (Nowack et al., 2013). Weathering can take place during the use phase and end of life, and is the result of a combination of mechanical, chemical, and thermal stressors, such as the exposure to UV light, to rain and moisture, to salinity, temperature, etc. Last, combustion can occur accidentally or as a controlled process such as the incineration of composites as municipal solid waste or as special waste. Depending on the characteristics of the combustion, such as temperature and oxygen levels, the fate of the composite will be different (Nowack et al., 2013).

Many studies focused on the release of particles from C-NM composites due to mechanical, chemical, and thermal processes (Duncan, 2015; Petersen et al., 2011; Kovochich et al., 2018), including a recent technical report (ISO-TR-22294:2021), reviewing and evaluating the utility of available methods to assess material release (for more detailed insights refer to ISO/TR 22293:2021 (2021).

The collected studies (see Supplementary File) used diverse equipment to simulate or perform the stress activity/ies, such as the Taber

Abraser machine (Netkueakul et al., 2020; Chortarea et al., 2022; Wohlleben et al., 2011), drilling machines (Neubauer and Wohlleben, 2017; Bello et al., 2010), belt sanders (Kang et al., 2017), or sanding paper (Wohlleben et al., 2012; Wohlleben et al., 2011) for abrasion, thermogravimetric analysis (TGA) system (Kotsilkov et al., 2018), cone calorimeters (Netkueakul et al., 2022; Chivas-Joly et al., 2014), combustion ovens (Bouillard et al., 2013), laboratory burners (Hufnagel et al., 2021), or steady state tube furnaces (Zhang et al., 2015) for combustion, and a combination of UV irradiation, acidic solutions, submersion, and climate chambers for weathering (ISO 3892–2:2006 and ISO 4892–2 are usually followed for UV irradiation and UV plus humidity cycles, respectively) (Rhiem et al., 2016; Wohlleben et al., 2012; Nguyen et al., 2017; Schlagenhauf et al., 2015). In addition to the variety in equipment, the experimental conditions (e.g. drilling speed, treatment time, combination of stressors) are often different among studies, which makes it difficult to do a systematic comparison. However, while standards for some of these release tests exist to improve the comparability of the results, in the real world these processes can be very different and unpredictable, as they are affected by external conditions that cannot be controlled (e.g. weathering or combustion), meaning that all studies represent potential real-life situations.

In addition to measuring the effect of the presence of the C-NM on the composite properties (which will determine its behavior when subjected to the stressors), the release of particles is studied in terms of number/amount, size (distribution), shape, presence of protruding or free NM, released chemicals (for combustion), and matrix degradation.

For combustion, often the focus is on the thermal properties of the material, such as its stability, and on the profile of released chemicals; therefore information about the C-NM fate is missing or not explicitly stated. However, on a general level if the composite goes through a full combustion the C-NM will be completely degraded, either as carbon dioxide in the presence of oxygen or as other organic or inorganic compounds in absence or scarce oxygenation (Kotsilkov et al., 2018; Dittrich et al., 2013; Sotiriou et al., 2016).

3.1. Classification of release data

The categorization of release information into low, medium, and high concern (green, yellow, and red) was based on the release of free nanomaterials from the composite, as an indicator of risk of exposure to the C-NM. Specifically, the three color codes indicate:

- Green (1): No free nano-fraction released;
- Yellow (2): No information about free NM, or free NM are detected via microscopy but not quantified or detected with quantitative methods;
- Red (3): there is a detectable nano-fraction released from the composite.

The release of free NM is the most direct way in which the use of nano-fillers may cause an additional risk of exposure for humans compared to the use of the matrix alone. The nano-fillers can however cause additional changes in the released particles, which could again determine a change in the exposure risk from the composite without nano-filler: the C-NM can be present as a protrusion on the surface of the composite particles (Kang et al., 2017; Saber et al., 2016; Hirth et al., 2013), which can change the interaction of the particles with biological systems; and/or the C-NM can change the amount and properties (size, shape) of the particles (or chemicals in the case of combustion) released, resulting in a change in exposure (Starost et al., 2017; Neubauer and Wohlleben, 2017). While we report this information in the next sections, we did not include these aspects in the classification criteria, on one side for the heterogeneity in the measuring of these indirect effects, and on the other side for the uncertainty in defining a threshold for these effects to be worth of concern.

3.2. Carbon black

Fig. 2 shows a synthesis of the information available about the release of particles from CB composites, and the classification of each combination of CB, matrix, and release process according to the criteria explained in Section 3.1.

CB has been used in combination with various thermoplastics, such as LDPE, Polyurethane, and polypropilene (PP); compared to the matrix alone, the same or a lower amount of particles were released during abrasion, and no change was observed in the size and shape of the particles, which were lumps of material (Ding et al., 2017; Neubauer and Wohlleben, 2017); free CB particles were observed with polyurethane matrix (Neubauer and Wohlleben, 2017), while LDPE matrix showed no release of free nanomaterials (Bott and Franz, 2019). LDPE showed no release of free CB particles even when the mechanical stress was coupled with chemical stress (immersion in isooctane) or thermal stress (-50 °C and 100 °C), or when abrasion was conducted after stretching (Bott and Franz, 2019).

Weathering was tested with a CB-polyurethane composite: UV light and simulated rain caused less degradation of the composite compared to the matrix alone, and the NM remained agglomerated on the composite surface. Free CB could be observed if, after the weathering, the composite was shaken (Wohlleben et al., 2016).

Regarding combustion, CB increased the thermal stability and flame retardant properties of the composite, thus requiring higher temperatures to fully decompose and generating less smoke and more char/residues (Zhou et al., 2019; Jakab and Omastová, 2005; Dittrich et al., 2013; Liu et al., 2016). During pyrolisis, a thermal degradation occurring in an inert atmosphere (no oxygen), a change in the profile of hydrocarbons released was observed for LDPE (Jakab and Omastová, 2005), while for PP the observations were not consistent between different studies (Dittrich et al., 2013; Jakab and Omastová, 2005). Alternatives to combustion are bioremediation processes using microorganisms to eliminate polymeric waste, which avoids the production of undesired combustion-derived residues. However, these processes have their own limitations, as described by Singh et al. (2017).

CB is used in paints as a black pigment; its use had no effect on the amount and size of particles released when the paint was abraded, and no CB alone was freed. Interestingly, the abrasion equipment was the source of dust in the nanometer range, rather than the material itself (Koponen et al., 2011; Saber et al., 2012; Koponen et al., 0120).

CB-rubber composites, which are used for tyres, did not show any release of free nanomaterial when subjected to multiple combinations of abrasion, chemical stress, stretching, and thermal stress (Bott and Franz, 2019).

Last, the weathering of CB-epoxy composites by UV and UV plus rain showed no change in the behavior of the matrix, with cracks appearing on the composite surface. The release of particles was similar or lower than the matrix alone, and only occasional free CB particles were observed (Zepp et al., 2020).

3.3. Carbon nanotubes

Fig. 3 shows a summary of the information about CNT-composites release. Due to the concerns about the bio-persistence of fibers, CNT release from composites has been widely studied.

Considering thermoplastics as matrices, no free CNT was released due to wet cutting, the standard process for composite processing (Bello et al., 2009), or due to abrasion (Wohlleben et al., 2012; Wohlleben et al., 2011; Anas et al., 2019), if the matrix is soft and elastic, the high temperature during sawing causes it to reflow around the CNTs, covering them (Ding et al., 2017); otherwise, the CNT can be occasionally found protruding from the matrix (Ding et al., 2017; Kang et al., 2017; Neubauer and Wohlleben, 2017). There is no agreement instead on the amount and shape of released particles, which depended on the specific matrix and on the abrasion procedure (Ding et al., 2017; Bossa

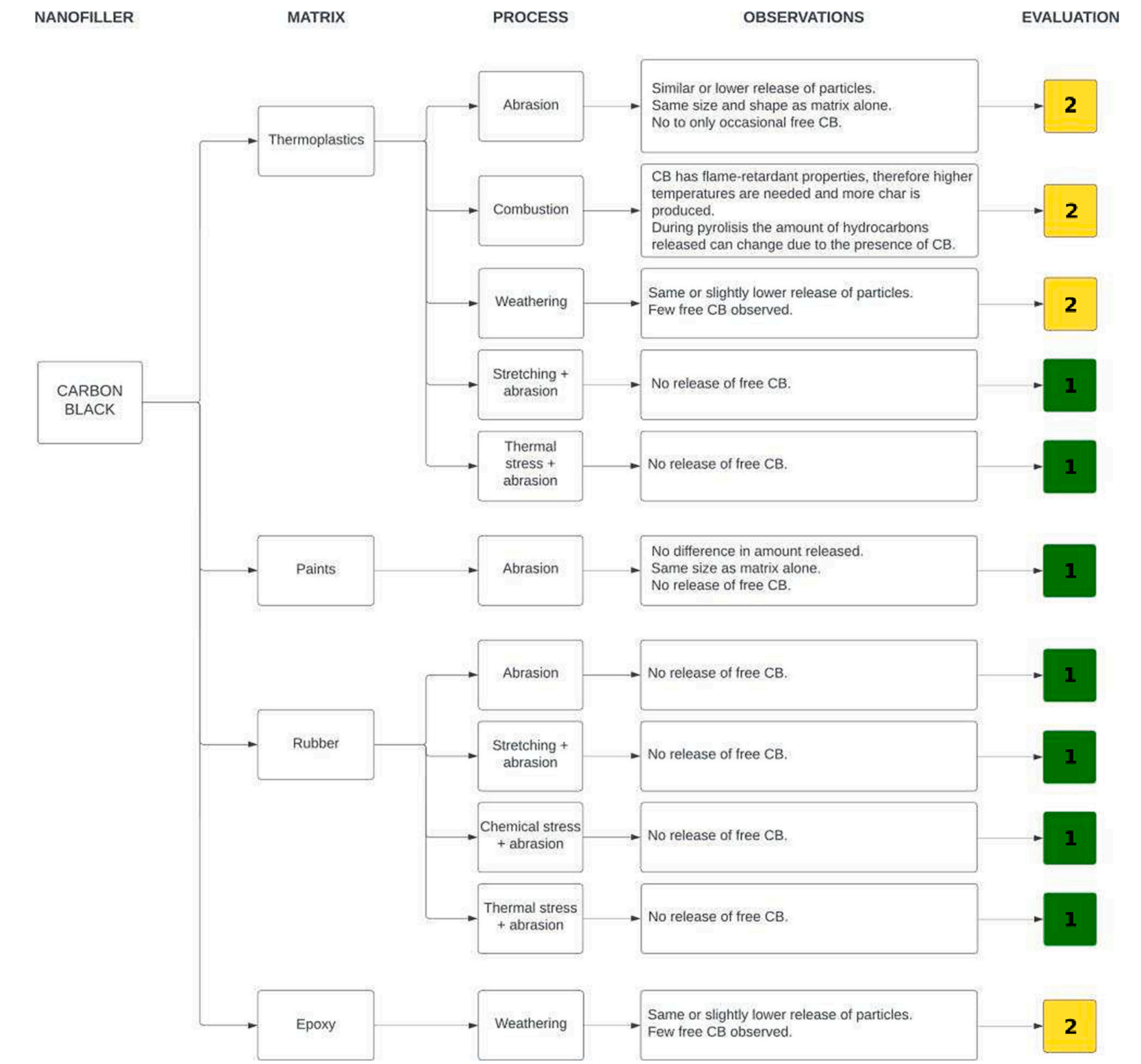

Fig. 2. A synthesis of the information available for CB on the release of particles from different combinations of matrices and stressors, and the classification in low (1, green), medium (2, yellow), and high concern (3, red) based on the release of free NM.

et al., 2021; Wohlleben et al., 2011; Wohlleben et al., 2012; Kang et al., 2017; Neubauer and Wohlleben, 2017).

CNT-thermoplastic composites show an improved thermal stability; if the higher decomposition onset temperatures were not reached, primary carbon particles and CNT were found as unburned or incompletely burned soot/ashes particles (Bouillard et al., 2013; Dittrich et al., 2013; Kotsilkov et al., 2018). The ventilation conditions affected the quantity of carbon monoxide and the type of hydrocarbons released, but not the nanomaterial fate (Zhang et al., 2015).

Exposed to UV light and simulated rain, the matrix of CNT-thermoplastic composites degraded, leaving the nanomaterial tangled on the surface exposed to the atmosphere. The CNT formed in this way a strong protective layer for the inner parts of the composite, reducing the subsequent release of matrix particles from the surface (Wohlleben et al., 2011; Wohlleben et al., 2012; Han et al., 2019). No free CNT was released, unless the composite was a thin layer such as a polypropylene (PP) film; in that case, even though reduced by the presence of the CNT, the weathering caused the composite to become brittle and create cracks that destroyed the structure of the film, thus releasing the CNT once the matrix was degraded to small pieces (Han et al., 2019). Moreover, further mechanical, chemical, and thermal stressors applied to CNT-thermoplastic composites can cause a level of degradation of the matrix up to the release of free and/or protruding CNT (Wohlleben et al., 2016; Rhiem et al., 2016).

A different case was observed if the composites were exposed to thermal and chemical stress or to weathering and then drilling: in both cases the CNT remained tangled in the matrix and were not released (Neubauer and Wohlleben, 2017; Kotsilkov et al., 2018).

Anti-corrosive paint with CNT exposed to UV light and then to sandblasting did not show any release of free CNT (Anas et al., 2019). No free CNT particles were observed as well for CNT-cement after abrasion and weathering, and very low to no degradation was observed due to the

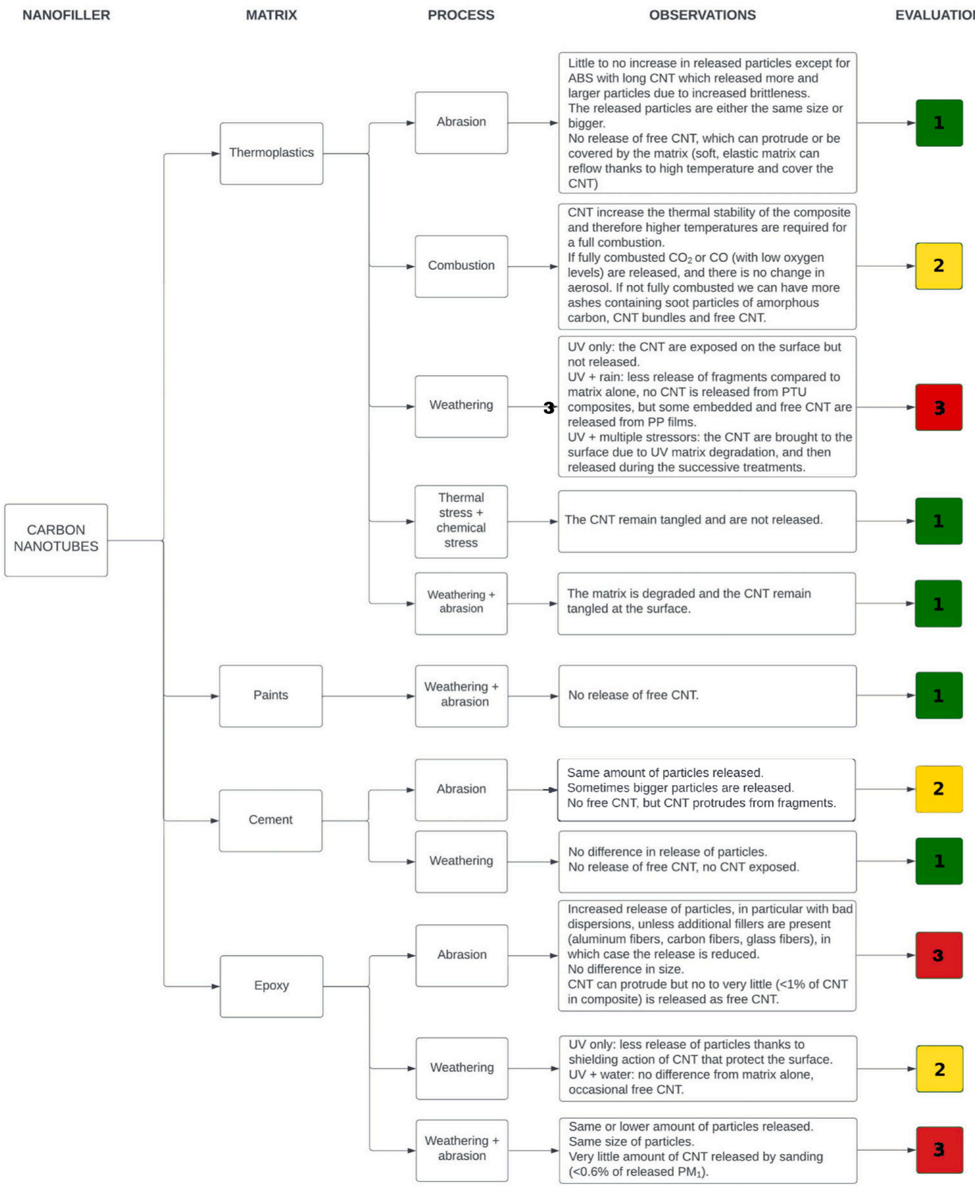

Fig. 3. A synthesis of the information available for CNT on the release of particles from different combinations of matrices and stressors, and the classification in low (1, green), medium (2, yellow), and high concern (3, red) based on the release of free NM.

hardness of the material; however, CNTs protruded from the fragments released through abrasion (Wohlleben et al., 2011).

For CNT-epoxy composites, an important factor affecting the response to abrasion is the quality of the dispersion: a poor dispersion resulted in a higher release of particles, while when the dispersion was good the release was reduced (Pras et al., 2020). However, the same or a higher amount of particles was observed (Pras et al., 2020; Gomez et al., 2014; Starost et al., 2017), unless an additional fillers were present to further reinforce the composite, such as alumina fibers, carbon fibers, and glass fibers, in which case the release was reduced compared to the matrix alone (Bello et al., 2010; Kang et al., 2017). CNTs protruded from the surface of the material, and Anas et al. (2019) measured that between 0.02% and 0.04% of the debris was constituted of free CNT, which amounted to less than 1% of the NM, and was proportional to the quantity of CNT (which was max 4% by weight).

The CNT had a protective effect on the epoxy composite when exposed to UV light, thanks to the reduced exposure of the matrix once the first layer was degraded and the CNT remained exposed (Zepp et al., 2020; Nguyen et al., 2017). When simulated rain was added, though, there was no significant difference with the matrix alone (Schlagenhauf et al., 2015; Zepp et al., 2020). Protruding and free CNT were observed regardless of the weathering process (Zepp et al., 2020). When weathering was combined with abrasion the same reduction in release was observed if only UV light was used for weathering, while the combination with rain resulted in a similar behavior of the composite and the matrix alone (Schlagenhauf et al., 2015; Petersen et al., 2014). 0.2% to 0.6% of the PM1 fraction of the released dust was composed of free CNT (Schlagenhauf et al., 2015).

3.4. Graphene-related materials

Fig. 4 reports a synthesis of the information available about the release of particles from composites with GBMs.

For GRMs, thermoplastics and epoxy have been considered as matrices. Abraded GRM-polyamide released more and smaller particles, which included rGO sheets alone due to the scarce adhesion between the filler and the matrix (Chortarea et al., 2022). Sanded GRM-polyurethane instead released less fragments than the matrix alone, and showed no

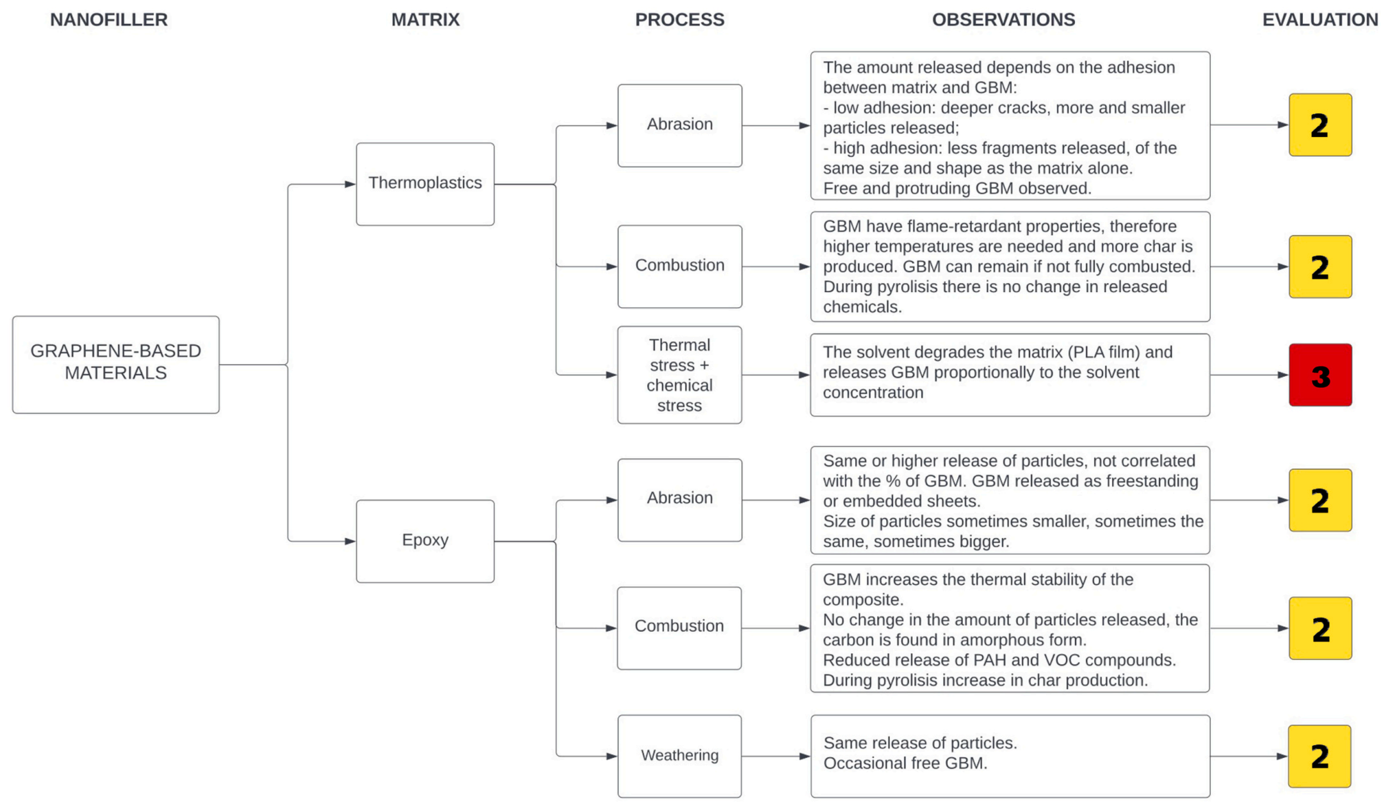

Fig. 4. A synthesis of the information available for GBM on the release of particles from different combinations of matrices and stressors, and the classification in low (1, green), medium (2, yellow), and high concern (3, red) based on the release of free NM.

change in particle size and no release of free graphene platelets (Neubauer and Wohlleben, 2017; Goodwin et al., 2020; Zepp et al., 2020).

When combusted, both polypropylene and poly(lactic) acid (PLA) films showed increased flame-retardant properties; this meant that if the higher temperatures needed for the full decomposition of the material were not reached, unburned GBMs could be found in the ashes, which were produced in higher quantities (Kotsilkov et al., 2018; Dittrich et al., 2013).

PLA films subjected to thermal plus chemical treatment were degraded by the ethanol solvent, causing a proportional release of the GRM (Kotsilkov et al., 2018).

The amount of "released" GRMs from GRM-epoxy composites was measured by labeling the nanomaterial with lead and measuring the lead released after the immersion of the abraded particles in HNO_3 (Hammer et al., 2020; Netkueakul et al., 2020). This method however does not discriminate between protruding and free GBMs, thus the presence of free GRM cannot be verified.

When exposed to weathering, the composite reacted in the same way as the matrix, with lower amounts of particles released when exposed to UV light alone, but the same if rain was simulated as well. Graphene sheets were however observed (Zepp et al., 2020; Goodwin et al., 2020).

Combustion showed the same pattern as for the other composites: increased thermal properties and depending on the temperature the carbon can be found in a different form, in this case as amorphous carbon (Netkueakul et al., 2022). Interestingly, the use of GRM reduced the emission of CO, polycyclic aromatic hydrocarbons (PAH), and volatile organic compounds (VOCs), which are known to have short- or long-term adverse effects on human health (Netkueakul et al., 2022; Wang et al., 2014).

4. Toxicity of released particles/substances

While the toxicity of pristine C-NM has been extensively studied (Devasena et al., 2021; Madannejad et al., 2019; Francis and Devasena, 2018), that is not the case for the toxicity of the particles produced by mechanical or chemical stress of C-NM composites, as of July 2022 we could identify only a low number of articles on the topic (see Supplementary Files). Abrasion was the main stress process considered, was the main stress process considered, while only six studies addressed weathering (2) and combustion processes (4) (Schlagenhauf et al., 2015; Hufnagel et al., 2021; Han et al., 2019; Netkueakul et al., 2022; Singh et al., 2017; Coyle et al., 2020).

Due to the concerns connected to the fiber pathogenicity paradigm (Kane et al., 2018), the majority of the studies concerned composites containing CNTs. The interest in the toxicity of particles released from GRM composites is more recent, with the identified studies published in the last two years.

For CB, we found information only on the toxicity of abraded paint, even though more than 92% of produced CB is used as filler in rubber composites (Fan et al., 2020). This is due to our goal of understanding the potential additional health impacts caused by the filler compared to the matrix alone. However, additives are always employed in rubber manufacturing, and in particular CB is a commonly-used reinforcing filler (Fan et al., 2020); for this reason, comparing the composite with the unfilled rubber is not relevant, as rubber without additives is not a viable option for the applications of the composite. The toxicity of particles released from rubber composites (especially tyres) is of concern, and is investigated without distinguishing the contribution of the single components (Poma et al., 2019; Kreider et al., 2020; Baensch-Baltruschat et al., 2020; Thornton Hampton et al., 2022; W.H. Organization et al., 2022). Those studies, though, fall outside our scope and are not included in this work.

Overall, most of the studies considering abrasion and weathering processes showed no difference between the C-NM composite and the matrix alone; while in certain cases the composite elicited no adverse response (Han et al., 2019; Netkueakul et al., 2020), in others comparable effects were observed for both the composite and the matrix alone, indicating no additional nano-specific effects (Schlagenhauf et al., 2015; Saber et al., 2016; Saber et al., 2012; Wohlleben et al., 2011). Transient nano-specific increase in LDH in Bronchoalveolar Lavage Fluid (BALF) and inflammatory RNA expression was observed in one case when particles from the abrasion of CNT-acrylonitrile butadiene styrene (ABS, a thermoplastic) were administered to mice via oropharingeal aspiration (Bishop et al., 2017). After 24 days, all markers had returned to baseline levels, indicating only acute effects. Interestingly, for CNTs and GBMs nano-specific effects were observed respectively in the liver of mice and on human intestinal epithelial cells (Caco-2). In the first case, the mice were administered the particles from abrasion of two different CNT-epoxy composites via intratracheal instillation, and even though no effect was observed in the lung, histological inflammation and necrotic changes were detected in the liver (Saber et al., 2016). In the second case, reduced graphene oxide (rGO)-polyamide 6 (PA6) abraded particles caused a reduction in cell viability at high concentrations (Chortarea et al., 2022). These studies seem to suggest that, despite the lung being the first organ in contact with the released particles, the digestive system might be a sensitive target; further research is therefore recommended.

In the case of particles released from abrasion of paint containing CB, Mikkelsen et al. (2013) found significant effects compared to the paint alone on HUVEC cells which could not be attributed only to the CB component. The release of LDH, even though not significant, was higher for the CB-paint that for the paint alone or CB alone; ICAM-1, a regulator of inflammation, was similar to pristine CB, while for oxidative stress the effects were higher than the paint alone but lower than CB. Considering that the paint contained only 2.5% CB in weight, it is improbable that effects similar or higher than the pristine CB are caused by the CB alone; replicating the experiment would be needed to understand the dose–response relationship. On the opposite, Saber et al. (2012) did not observe any nano-specific effect of abraded particles of CB-acrylic paint, both *in vitro* and *in vivo*.

The toxicity of particles released by the combustion of nanocomposites represents a different case than abrasion and weathering; in fact, depending on the temperatures, the C-NM is partially or completely decomposed in amorphous carbon or carbon dioxide (Liu et al., 2016; Dittrich et al., 2013; Kotsilkov et al., 2018). Moreover, multiple organic and inorganic compounds can be released, depending on the material and the combustion conditions (temperatures, oxygen levels,…). Potential adverse effects caused by the use of C-NMs in composites can therefore be linked to: a) release of NMs; b) release of amorphous carbon; c) change in type and/or quantity of produced organic and inorganic compounds (Netkueakul et al., 2022; Wang et al., 2014; Kotsilkov et al., 2018). Netkueakul et al. (2022) did not find any nano-specific effect on A549 lung epithelial cells considering a GRM-epoxy composite, even though both composite and matrix caused a response linked to the production of polycyclic aromatic hydrocarbons (PAH). Differently, Hufnagel et al. (2021) observed increased cytokine release in A549 cells exposed to combusted CNT-PE composites; since the CNT are expected to be completely combusted, this nano-specific effect is attributed to the presence of trace metals as impurities in the composite. Cytotoxic effects were instead caused by the released gases, such as Volatile Organic Compounds (VOC), but interestingly in this case the presence of the nanofiller resulted in a lower cytotoxicity, indicating that the C-NMS can as well reduce the toxicity of the composite thanks to changes in the material properties and composition. Increased cytotoxic effects were observed from combusted CNT-Polycarbonate composites, while CNT-Polyurethane composites showed no effect or significant effects in different studies (Singh et al., 2017; Coyle et al., 2020); in all cases, the effects were not caused by the nanofillers, which were completely decomposed, but by an increase in the amount of PAH produced during combustion.

While the above-mentioned works were conducted *in vitro* or *in vivo*, occupational studies can provide more direct information about the effects of nanofillers on workers. Most occupational studies focus on workers' responses to C-NM exposure in production facilities, where pristine nanomaterials are synthesized and handled. A review from 2019 identified 17 articles investigating the occupational toxicity of C-NM, specifically carbon black, multi-walled CNT (MWCNT), CNT and carbon nano-fibers (CNF) (Schulte et al., 2019). Overall, both CB and CNT appear to be inflammogenic, even though limited information about environmental and internal concentrations prevents the identification of a clear dose–response relationship (Schulte et al., 2019; Coyle et al., 2020). Initiatives such as the EU-Life project NanoExplore are defining harmonized protocols for the study of the effect of nanotechnology exposure on workers' health, and we can therefore expect in the future more high-quality comparable studies addressing occupational health of NMs (Guseva Canu et al., 2023).

A set of studies has specifically addressed the health of workers producing nanocomposites, considering the welding, smelting, and machining operations (Pelclova et al., 2018; Pelclova et al., 2018; Pelclova et al., 2020); while nano-SiO_2 was the main nanomaterial used, over the three-year monitoring time fillers from recycled carbon fibers were used as well (in the second year). The long-term study showed stable levels of oxidative stress during the 3 years, without cumulative effects nor adaptation; the levels were however higher than the control group. The chronic effects on workers decreased over time, even though such effects might be due to reduced exposure and behavioral change; however, the marker 8-OHdG was elevated during all the 3 years, which calls for attention due to the similarity of the exhaled breath condensate (EBC) findings and those of patients with silicosis and asbestosis (Pelclova et al., 2020). Based on the sensitivity of the different biomarkers, the EBC and plasma were identified as ideal fluids for the bio-monitoring of oxidative stress. Interestingly, though, the studies highlighted the fact that the majority of the nanoparticles were represented not by the nanofiller, but by the particles produced during the operations due to abrasion and hot temperatures, such as iron and manganese-based particles. Organic chemicals might be released as well during the procedures. It is therefore difficult to pinpoint which substance (or combination of substances) is causing the adverse effects (Pelclova et al., 2018).

Overall, available occupational studies have a limited coverage of the topic investigated in this paper, both due to the focus on the production of NMs rather than nano-composites, but also for the difficulty in discriminating the specific effect of the nano-filler. This however pushes us to consider the potential toxicity of nano-composites in an holistic way, highlighting the complexity of real scenarios.

4.1. Classification of toxicity data

The hazard information was classified into three categories (green, yellow, and red) that reflected both the identification of additional effects compared to the matrix alone and the quality and quantity of available data (Table 1); specifically:

- Green (1): No additional effects compared to the matrix alone are observed in toxicological studies. Only one study is accepted if conducted *in vivo*, but if only *in vitro* data is available, at least two independent studies which tested for cytotoxicity, ROS production, and inflammation endpoints (in line with the oxidative stress paradigm (Shvedova et al., 2012)) are required;
- Yellow (2): No additional effects are observed, but the pool of data is not strong enough to classify as green: e.g. only one *in vitro* study is available, not all endpoints are tested…
- Red (3): Additional effects compared to the matrix alone are observed in at least one study.

The classification procedure confirms the scarcity of toxicity information, especially from multiple independent studies, which results in weak evidence of both presence and absence of nano-specific effects.

Table 1
Summary of the studies investigating the effects of the particles released from C-NM composites by use- and end-of life processes, and classification of the information according to evidence of additional effects compared to the matrix alone. VV = *in vivo* data, VT = *in vitro* data. *a*: No effects on the lung, but effects on the liver *in vivo*; *b*: Only acute effects *in vivo* but no effects long-term; *c*: The CNT are not expected to be found after combustion, and the negative effects are suggested to be caused by heavy metals present as impurities and VOC and PAH compounds.

Filler	Matrix	Process	Data availability	Difference from matrix alone (# studies)	Class
CB	Paint	Abrasion	VV + VT	YES (1/3)	3
CNT	Cement	Abrasion	VV	NO (1/1)	1
CNT	Epoxy	Abrasion	VV + VT	YES (1/3)[a]	3
CNT	Epoxy	Weathering + Abrasion	VT	NO (1/1)	2
CNT	Thermoplastics	Abrasion	VV + VT	YES (1/3)[b]	2
CNT	Thermoplastics	Combustion	VT	YES (3/3)[c]	3
CNT	Thermoplastics	Weathering	VT	NO (1/1)	2
GBM	Epoxy	Abrasion	VT	NO (1/1)	2
GBM	Epoxy	Combustion	VT	NO (1/1)	2
GBM	Thermoplastics	Abrasion	VV + VT	YES (1/1)[a]	3

5. Conclusions

In this review, we have drawn a picture of the status of the knowledge about C-NM composites and their behavior and potential hazard when subjected to mechanical, chemical, and thermal stresses during their production, use, and end of life. We focused in particular on the additional risks that the use of nano-fillers might pose, both in terms of release and toxicity.

We adopted a semi-quantitative approach to classify the available information in three levels of concern based not only on the results of the studies but also on their quality and completeness.

Fig. 5 shows a synthesis of our analysis. While the picture gives an idea of the filler-matrix combinations that might require more attention and further investigation, the potential risk of the composites is strictly correlated with the type of application the composite is used for and not primarily by its release and toxicity.

Concerning the release, the amount of free particles was quantified only in a few studies, but free NM were qualitatively observed for most of the composites, except for the paints, rubber, and cement, which did not show any release in any of the combination of stressors tested. For the other matrices, weathering and a combination of thermal, chemical, and mechanical processes was particularly critical, as the material was subjected to subsequent different kinds of stressors. Through these processes, the matrix can be degraded and the exposed nanofiller released. This type of situations can occur during the use phase of a product, for example if the material is exposed to the weather or if it is used as a food container, or during the end of life, for example in a landfill. Depending on the use, humans or the environment might be the closest target, and a proper risk assessment should be conducted to verify the risks (e.g. a playground where the composites are exposed to the weather and kids play will be a different situation that the landfilling of the composite). For weathering, the type of matrix and the thickness of the composite are factors that play a major role for the fate of the filler, since if the matrix is easily degraded the whole composite will lose its structural stability (Zepp et al., 2020).

The recycling of C-NM reinforced polymers was not the main topic of this review, although some studies reported that during recycling of

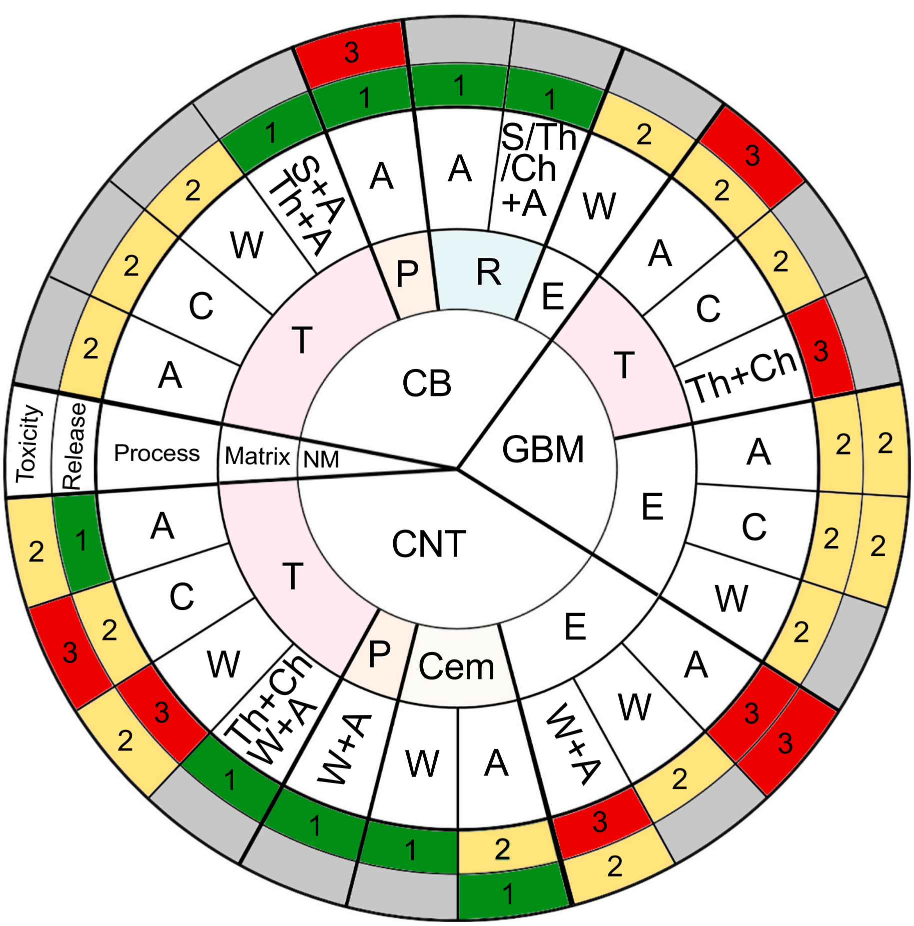

Fig. 5. Overview of the classification of release and toxicity information (as of July 2022). For the matrix: T = thermoplastics; P = paints; R = rubber; E = epoxy; Cem = cement. For the processes: A = abrasion; C = combustion; W = weathering; S = stretching; Th = thermal stress; Ch = chemical stress. Green (1): no free NM released (for release) or no nano-specific effect verified *in vivo* or with multiple *in vitro* tests (for toxicity). Yellow (2): Free NM detected only qualitatively or not investigated (for release), or too few studies showing no nano-effect (for toxicity). Red (3): free NM detected with a quantitative method (for release) or additional nano-effect observed (for toxicity), Grey: no data available.

CNT-PC (Boonruksa et al., 2017) or CNT-PP (Boonruksa et al., 2016), airborne particles were released, but no free CNT were found in any processes. This is in line with abrasion data summarized here.

For no composite the toxicity data were complete enough to show with good reliability that there are no nano-specific effects when adding C-NM as fillers. Moreover, this topic is still in an early phase, as demonstrated by the many C-NM-matrix-stressors combinations that have not yet being tested, and by the extremely limited availability of occupational studies.

The combustion process showed a peculiar consistency regardless of the matrix and C-NM considered. In all cases the thermal stability was increased and unburnt NM could be released if the higher temperatures needed to fully decompose the nanofiller were not reached. This calls for attention especially for incineration plants, where adaptations in the combustion process could be implemented, or the ashes containing free NM could be properly managed and disposed of, not to pose a risk to workers and the general population. Moreover, the change in production of hazardous chemicals should be addressed as well, as the use of C-NM could cause non-nano-specific additional risks or conversely reduce the release of e.g. VOCs and PAH.

Last, an additional consideration should be made: C-NM fillers are being used in composites due to the improvements they bring in properties and functionality. The potential risks should be put into context with the additional benefits these materials provide, and be benchmarked against their alternatives, with a comprehensive evaluation of the impacts generated by choosing one option over the other.

CRediT authorship contribution statement

Daina Romeo: Conceptualization, Formal-analysis, Data-curation, Writing-original-draft. **Pietro Clement:** Conceptualization, Investigation, Data-curation, Writing-review-editing. **Peter Wick:** Conceptualization, Writing-review-editing, Supervision, Funding-acquisition.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, athttps://doi.org/10.1016/j.impact.2023.100477.

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