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Article

Release of Graphene and Carbon Nanotubes from Biodegradable Poly(Lactic Acid) Films during Degradation and Combustion: Risk Associated with the End-of-Life of Nanocomposite Food Packaging Materials

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Abstract: Nanoparticles of graphene and carbon nanotubes are attractive materials for improvement of mechanical and barrier properties and functionality of biodegradable polymers for food packaging applications. However, the increase of the manufacture and consumption increases the probability of exposure of human and environment to such nanomaterials, this rising questions about the risks of nanomaterials since they can be toxic. For a risk assessment, it is crucial to know whether airborne nanoparticles of graphene and carbon nanotubes can be released from nanocomposites into the environment at their end-life, or they remain embedded in the matrix. In this work the release of graphene and carbon nanotubes from the poly(lactic) acid nanocomposite films were studied for the scenarios of: (i) biodegradation of matrix polymer at the disposal of wastes; and (ii) combustion and fire of nanocomposite wastes. Thermogravimetric analysis in air atmosphere, TEM, AFM and SEM were used to verify the release of nanoparticles from nanocomposite films. The three factors model was applied for the quantitative and qualitative risk assessment to the release of graphene and carbon nanotubes from nanocomposite wastes for these scenarios. Safety concern is discussed in respect to the existing regulations for nanowastes stream.

Keywords: graphene; carbon nanotubes; poly(lactic) acid, degradation, combustion, fire, risk analysis.

1. Introduction

Manufactured nanomaterials are applied in various consumer goods in order to enhance their properties or supplement to novel functionalities. The industry has already utilized nanoclays, metal nanoparticles and carbon nanotubes and has managed to use them in products for variety of applications, e.g. semiconductors, automotive, aerospace, electronics, energy, defense, sporting goods and packaging [1]. Nanotechnology allows the scientists to alter the structure of packaged materials on a molecular scale in order to give the materials desired properties [2,3]. Nowadays, different types of carbon nanotubes and graphene in polymer nanocomposites are widely investigated for the development of smart, active and intelligent packaging that can improve the quality and safety of food, to solve the food storage problem and inform the consumer for the quality of packaged food [2-4]. Graphene and multiwall carbon nanotubes (MWCNTs) in biodegradable polymers are the most continuous and potentially valuable nanoscale materials to have emerged in

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recent years that are increasingly studies to enhance thermal, mechanical, barrier properties and functionality of food packaging materials [1-3, 5]. Graphene and its derivatives are identified as powerful candidates for gas-barrier materials because perfect graphene does not allow the diffusion of small gases through its plane [6-8]. Incorporation of graphene and carbon nanotubes into polymer matrices are promising nanotechnology approach also to increase mechanical strength and improve thermal properties when properly dispersed in a polymer matrix [9,10].

At the same time regulations at national, EU and international level are still struggling to agree upon unified and mutually accepted definition of a "nanomaterial". As the market of nanomaterial-based products is expected to triple by the year 2020 in more industrial sectors, the application of nanomaterials and nanoparticles is expected to grow proportionally [2,3,11]. As a result, environmental exposure to nanoparticles in air, water and soils is also expected to increase [11]. Therefore, more research efforts in nanoscience are needed to focus exclusively on the potential risk of nanomaterials graphene and carbon nanotubes with the increasing exposition of consumers and environment to nanoparticle-containing food packaging. The specific nanoscale size and shape of graphene and carbon nanotubes with large aspect ratio and large surface area, airborne, non-soluble in water and absorptive in soil, will enhance the risk for their mobility in the environment [12,13].

Currently, very little is known about the release of nanomaterials graphene and carbon nanotubes (CNT) incorporated in polymer nanocomposites. Although they are typically tightly bound in the matrix polymer, their release through the lifecycle of nanocomposite is possible [11]. Therefore, greater information is needed on the potential hazard associated with specific exposure scenarios. Few scenarios were identified and published in the literature [11,14,15] where CNTs might be released into the environment during the life cycle of polymer nanocomposites, in production, service life and disposal stages. The authors found that there are currently no standard methods to measure what is released from use of products containing nanomaterials. Researchers [16,17] reviewed the potential release of CNTs into the environment during the service life where untrained humans are in contact with oil-based polymer nanocomposites. They considered three possible pathways for release of CNTs: due to exploitation and use, degradation of the matrix due to weathering processes, and fire events. Duncan and Pillai [18] considered two nanoparticle release paradigms: (i) via passive diffusion, desorption and dissolution into external liquid media; and (ii) by matrix degradation. However, study on the release of graphene is found only for the production stage [12]. Release during service life of MWCNT-based composites is projected to be quite low and composed of polydisperse fragments with only a small fraction of free MWCNTs [15-17]. Studies for the release of graphene from food packaging materials into food are very scare [19-21].

If consider the end of life phase, after direct disposal such nanomaterials may occur in waste depots, waste landfills, or wastewater, where they can leak into the soils and ground water, or be released into the air. For most materials, degradation of the polymer matrix is associated with the greatest potential for release, with degradation and release rates dependent on the specific characteristics of the polymer, CNTs, and environment [15,16]. Authors agree that the CNTs form a network and are not easily detachable from the samples. However, the formed CNT layer on the surface of degraded composites could be a source of a high quantity of released free standing CNTs and thus maybe pose a health risk [16,17]. The degradation of the biopolymer in erosion or composting creates a potential for the nanoparticles embedded in the composite to be partially or completely released from the polymer [18]. Thus, the nanoparticles would be able to pass into the air or to engage in soil and groundwater [22]. However, insufficient information can be found for the release and fate of graphene due to partial degradation of composite biopolymers.

End-of-life aspects of nanomaterials have received far less attention than their preparation or application [23]. The two main strategies used for the end-of-life of thermoplastics products are recycling and burning to produce energy (thermal valorization). As the release of nanoparticles during grinding of nanocomposite wastes presents a potential risk, the incineration of nanocomposites is recently accepted as a prospective waste management strategy, for which nanoparticle emission during burning must be addressed as a premise. So far, no detailed study has been published that investigates the release of graphene from nanocomposites due to accident fire or

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burning. Few publications discuss the incineration and burning of CNT-based nanocomposites [24,25]. In contrary to incineration where under high temperatures CNTs can be destroyed [24], a fire or burning of CNT nanocomposites in open air may not degrade all CNTs particles in composites, since the decomposition temperature of CNTs is much higher, than of the polymer matrix. A network of CNTs is formed in the char (residue ash), but measurements are still missing if CNTs can be released from the residue ash into the air. Bouillard at all. [25] reported on the release of free CNTs and agglomerates of CNTs from ABS nanocomposites into air during nanowaste combustion at quite low temperatures (about 400 $^{\circ}$C). This information is important to assess the environmental risks and the inhalation risks to people engaged in those practices.

In the present study we address these issues based on the examples of graphene nanoplatelets (GNP) and multi-walled carbon nanotubes (MWCNTs) incorporated in biodegradable poly(lactic) acid (PLA) polymer composites. We investigate the release of graphene and carbon nanotubes from biodegradable poly(lactic) acid nanocomposite films during polymer degradation and burning at various temperatures. We analyze the risk from release of graphene nanoplatelets and MWCNTs associated with the end-of-life of nanocomposite food packaging materials to human and environment by applying a three-factor method (C.E.L.) for risk assessment. Safety concerns were discussed in respect to the existing regulations for application of nanomaterials in food packaging.

2. Materials and Methods

Nanocomposite of poly(lactic) acid polymer (PLA) filed with graphene nanoplatelets (GNP) and multiwall carbon nanotubes (MWCNTs) in form of filament for 3D printing (FDM) was supplied from Graphene 3D Lab, USA. Commercial neat PLA filament was also supplied. Disk samples were 3D prepared layer-by-layer with X400 Rep Rap printer (FDM), with dual extruders, forming sandwich structure of 10 alternative layers of nanocomposite and PLA. The printed disk samples were hot pressed to thin films with thickness of 30 microns. The amount of nanocarbon filler in the final film samples is of 3 wt%.

Ultra-strong migration test was performed by heating of 90°C for 4 hours following by storage of 10 days at 40°C with dynamic treatment for 1 min per day. Samples were emerged in three aqueous-based solvents of 3 vol.% acetic acid, 10 vol.% ethanol and 50 vol.% ethanol. The migration test regime simulate the conditions of high temperature treatment of food packaging during service life [7], as well as during end-of-life as waste disposal.

Different visualization techniques were applied in order to identify migrants in the simulant media and to verify the film integrity after the migration test. The High-Resolution Transmission Electron Microscope (TEM) at accelerating voltage 200 kV and Atom Force Microscopy (AFM) Ambios, USA were used for analysis of the dried colloids of migrated substances into the surrounding solvents. For preparation of the test samples, a micro-quantity of colloid after migration test was dropped on copper TEM grid covered by a membrane from amorphous carbon (or on glass plate for AFM scan), and after that dried in a dust-free atmosphere at ambient conditions. While, the morphology of the film surface before and after migration test was studied by scanning electron microscope (SEM) Philips 515 with accelerating voltage 25 kV and 5 kV. Before the examination in the microscope, the samples were covered with metal coating for better conductivity of the surface and to avoid the discharge effects.

Thermal stability and degradation of nanocomposite films was studied by thermogravimetric analysis (TGA, Q50, TA Instruments) at 10°C/min in three different temperatures, from 30°C to 500, 650 and 850 $^{\circ}$C. The mass loss during heating and the amount of residue ash were analyzed. TEM was performed for analysis of the residue ash after burning at the three temperatures.

Risk assessment analysis was performed by the three factors method, 3F or C.E.L., i.e. grading the three risk analysis factors: Consequences (C), Exposure (E), and Probability/Likelihood (L).

3. Results and Discussions

3.1. Release of graphene and carbon nanotubes due to degradation of PLA polymer

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The use of biodegradable packaging materials will contribute to sustainability and reduction of wastes via degradation [26,27]. Composting, for example, has the potential to transfer biodegradable waste, including biodegradable plastics, into useful soil amendment products by an accelerated degradation using a mixed microbial population in a moist, warm, aerobic environment under controlled conditions. Song at all [26] found that biodegradable packaging materials are most suitable for single-use disposable applications where the post-consumer waste can be locally composted. However, special care should then be taken while handling local composting of biodegradable nanowastes to limit potential environmental risks due to release of nanoparticles in the soil from the compost.

We discuss herewith if the GNP and MWCNTs release as single nanoparticles or large aggregates from the nanocomposite packaging films via degradation of PLA matrix. The characterization of such release provides critical information for environmental nanoobject exposure from biodegradable nanocomposites. In our previous studies [19-21], we have investigated the release of GNP and MWCNTs from the composite film GNP/MWCNT/PLA in alcoholic and acid food simulants, high temperature migration conditions, such as: (i) strong static migration test (with heating at 90°C for 4 hours); and (ii) ultra-strong dynamic migration test (heating at 90°C for 4 hours followed by subsequent storage for 10 days at 40°C, including dynamic treatment for 1 min daily). The strong static and ultra-strong dynamic migration conditions were set accordingly with the prescription in EU Regulation 10/2011 (EU 2011) [28] and literature sources [29,30] for migration of polymer films in food simulants.

At the strong static migration test [19,20], we have observed that large graphene nanoplatelets (GNP) of about 100–1000 nm in length and a few nanometers in thickness indeed migrate from the poly(lactic) composite film, GNP/MWCNT/PLA, into food simulants. We have assumed that heating above the glass transition temperature enhance the dynamics of polymer molecules and facilitate the diffusion of graphene nanoplatelets from PLA film into food simulant. The migration conditions simulate the high temperature treatment of packaged food, including microwaving. The fibrous MWCNTs form entangled network in the PLA matrix, which prevent their release from the film surfaces when the PLA matrix degrade. In general, the total amount of released substances (nanoparticles and organic matter) from the composite GNP/MWCNT/PLA films is ranged within 0.028-0.053 mg/cm^2, depending on the type of food simulant, while the nanoparticle migrants were estimated around 0.006 – 0.011 mg/cm^2. The largest release of substances was observed in 3% acidic acid, followed by 50% ethanol, while the lowest release values are obtained in 10% ethanol. But, the released organic substances and particularly the number of released nanoparticles remain much lower than the Overall Migration Limit (OEL = 0.10 mg/cm^2) for substances released from food contact material, accepted by EU regulatory documents [28,31].

By contrast, during ultra-strong dynamic migration test [20] the release of nanoscale size particles (100 – 1000 nm) from the GNP/MWCNT/PLA composite film is higher (0.5–0.7 number %) compared to (0.1-0.2 number %) nanoparticle migrants that was observed during the strong static migration test in the three food simulants, 3% acidic acid, 10% and 50% ethanol. The larger size nanoparticle migrants (1 – 10 microns) were found also in higher amount (3 - 5 number %) during the ultra-strong migration test, compared to 1-2 number % for the strong static test. This was associated with partial degradation of the PLA polymer matrix, which support the diffusion of GNPs together with dissolved organic substances out of the film. In contrast, the MWCNTs form entangled network in the polymer film, which prevents their migration into food simulants if the polymer partially degrades. Importantly, the released nanoscale particles are ten-fold lower amount than the micron scale one.

In the present study, we use the results obtained above in order to discuss the scenario of nanoparticle release due to the degradation of GNP/MWCNT/PLA composite films at the end-of-life stage of disposal or composting the wastes. Figure 1 presents the TEM micrographs (a,b) and AFM scans (c,d) of the dried surrounding solvent of 10 % and 50 % ethanol after ultra-strong dynamic migration test. In Fig 1(e,f) the SEM micrographs of the film surfaces after such treatment.

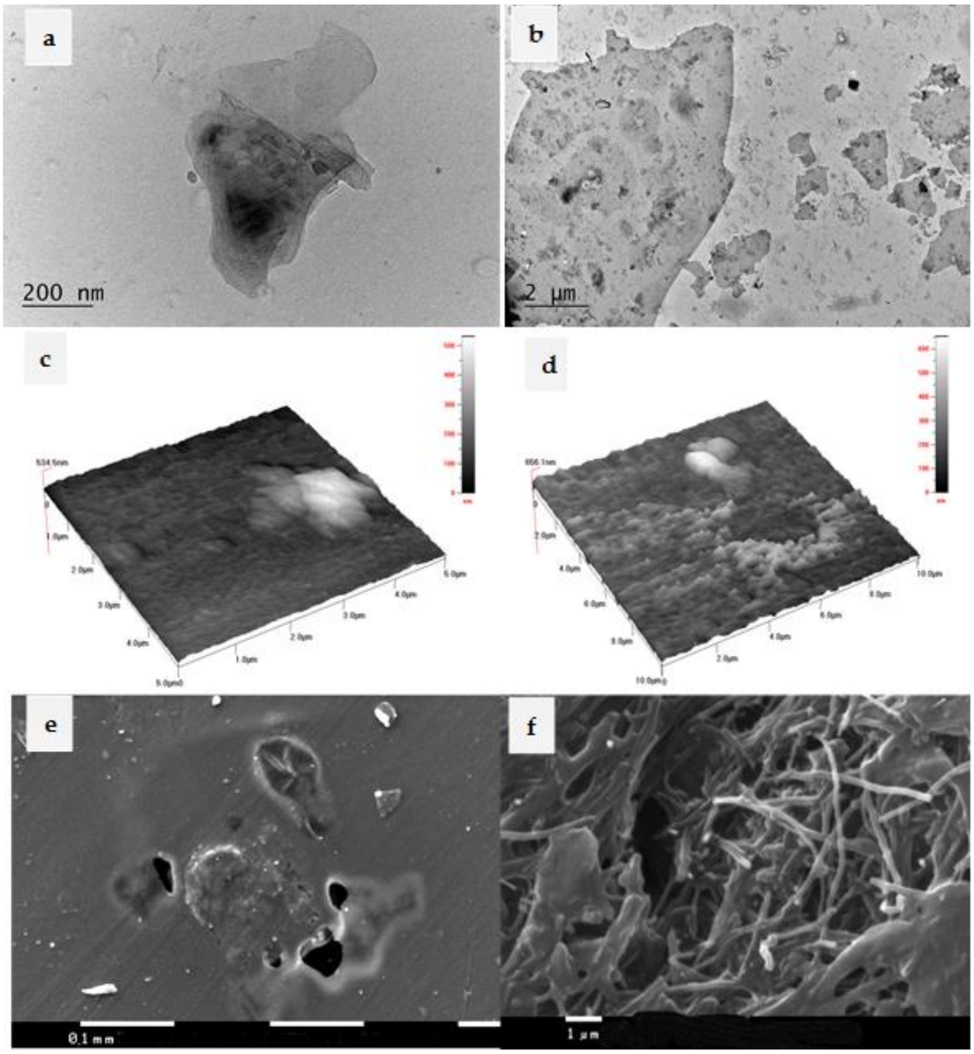

Fig. 1. (a,b) TEM micrographs and (c,d) AFM scan of migrants from GNP/MWCNT/PLA film in dried food simulants; (e,f) SEM micrographs of the film surfaces after the ultra-strong dynamic test into 10% ethanol (first column), and 50 % ethanol (second column).

As seen from Fig. 1 (a-d), the released graphene particles due to polymer degradation during ultra-strong dynamic time-temperature test may be classified in two groups: the nanoscale particles and the micron scale aggregates. The TEM micrographs in Fig. 1(a,b) demonstrate, that in 10% ethanol (a) mainly small aggregates of GNPs of the nanoscale size below 500 nm are observed in a low amount. However, in 50% ethanol (b), the amount of the released GNPs increases apparently, and the most of particles are in nanoscale size, 100-1000 nm. Only few aggregates of size 1 - 10 μm are visible in Fig 1(b). The AFM scans of dried colloids in Fig. 1(d), visualize the presence of many small objects with nanoscale size below 500 nm and a large aggregate of ~ 2 μm length and thickness of ~ 500 nm in 50% ethanol. While, in 10% ethanol (Fig 1c), the overall released particles, are of smaller amount and size about 1 μm. Importantly, MWCNTs are not visible to release from the GNP/MWCNT/PLA nanocomposite films, as observed by TEM and AFM analysis. Following the release mechanisms of nanoparticles proposed by Duncan and Pillai [18], we assume that the physical changes of biodegradable PLA polymer due to polymer hydrolysis provokes a diffusion of the dissolved organic substances doped with graphene nanoparticles, out of the film into the food simulant.

SEM analysis was performed in order to examine the film integrity after the ultra-strong dynamic migration test in the two alcohol-based simulants. For the films immersed in 10% ethanol, a few holes of size above 10 μm are visible on the film surface in Fig. 1(e), indicating the diffusion of the dissolved PLA organic substances and nanoparticles from the bulk. By contrast, in 50% ethanol

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the integrity of the GNP/MWCNT/PLA composite film is destroyed due to partial degradation of the PLA polymer on the film surface (Fig. 1f). It is visible that the fibrous MWCNTs formed an entangled network as the PLA polymer matrix dissolves, which prevent their release into the food simulant.

Therefore, if biodegradable nanocomposites waste containing GNPs and MWCNTs are disposed in landfills, nanoscale graphene platelets can certainly be released in the environment due to partial degradation and weathering. If such nanowastes are added for composting, the biodegradation process provides compost that is very likely to contain large amounts of nanoscale GNPs (100-1000 nm), as well as graphene aggregates and bundles of carbon nanotubes of micron size (1-10 μm). Since the compost is intended to be used for soil improvement, the nanoparticles will penetrate into soil and groundwater and there is a risk that they will fall into the food chain of different organisms.

3.2. Release of graphene and carbon nanotubes due to burning of nanowastes

Burning of nanocomposite wastes to produce energy (thermal valorization) is recently discussed as a nanowaste management strategy, thus the risks for nanoparticle emission during incineration of thermoplastic nanocomposites must be addressed and investigated [25]. Moreover, the treatment of such waste by accident fire or burning in landfills (a common practice in underdeveloped regions), may pose questions associated with environmental and human risks due to potential releases of large amounts of nanoparticles into the environment. In principle, graphene and CNTs are combustible materials above 600^{o}C, and they can be easily transformed into CO/CO2 during combustion [25]. The published results on this subject are very scarce, but few papers [32-34] reported that the combustion of polymer composites with CNTs could form residues (ashes) containing unburned CNTs. Moreover, the CNTs also may release in the combustion gas phase [25]. Therefore, in the present work we classify burning of nanowastes as a scenario that may have a greater possibility to release airborne nanoparticles. The characterization of such release may provide critical information for environmental and human accidental nanoparticle exposures.

Thermogravimetric analysis (TGA) was performed to simulate the nanowaste combustion in three heating regimes: 30 - 500 ^{o}C, 30 - 650 ^{o}C and 30 - 850^{o}C, at heating rate 10^{o}C/min in air atmosphere. The thermal decomposition of the neat PLA and the nanocomposite films (GNP/MWCNT/PLA) was analyzed by weight loss (%) versus temperature (^{o}C), as shown in Fig. 2. The thermal stability was determined from the onset of weight loss (T_{onset}). The decomposition peak temperature T_p and the residue ash were evaluated from the TG curves and data are presented in Table 1. The onset temperature (T_{onset}) of nanocomposite is observed around 230^{o}C and the decomposition temperature at 360 - 362 °C. The neat PLA show T_{onset} and T_p at lower temperatures, of 10^{o}C and 5^{o}C, respectively, this indicating that the thermal stability of PLA is improved by addition of 3 wt% mixed nanofillers, GNP and MWCNTs. As might be expected, the weight loss increases with increasing the heating temperature (T_{max}) from 500 to 850^{o}C. The combustion of the neat PLA at 500 ^{o}C results in 0.3% residue ash from the initial weigh of the sample consisting of amorphous carbon. However, the combustion of GNP/MWCNT/PLA form residues containing mostly unburned nanoparticles, GNP and MWCNT in amount of 3.3% at 500^{o}C, 1.5% at 650^{o}C and 0.07% at 850^{o}C, from the initial weigh of the sample, this confirming the results reported in few other studies [25,32-34]. Therefore, further potential environmental problems may arise with handling such residues. Our study advances the observations in [32-34] by showing that the amount of GNPs and MWCNTs in the residue ash decreases by increasing the burning temperature, this indicating for increased decomposition of carbon nanoparticles by controlled incineration/combustion temperatures.

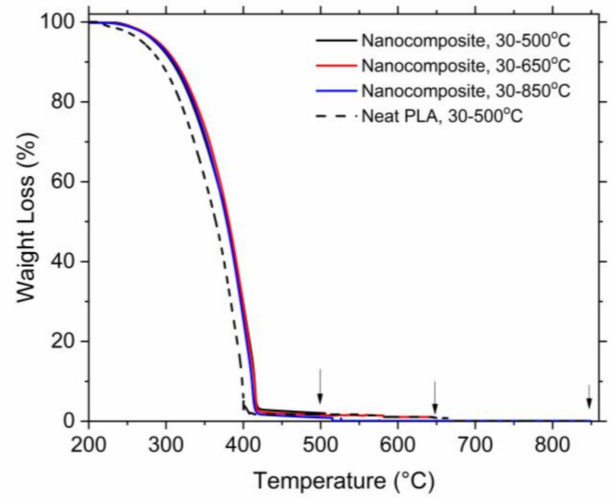

Fig.2. TGA measurements of GNP/MWCNT/PLA nanocomposite film compared to the neat PLA at three temperature regimes, 500, 650 and 850oC, in an air atmosphere

Table 1. Thermal characteristics of PLA and GNP/MWCNT/PLA nanocomposite by TG analysis

Sample	**Temperature of burning T_{max}**	**$T_{onset,}$ °C**	**T_P, °C**	**Weight loss, % at T_{max}**	**Residue ash, %**
Neat PLA	500 ^{o}C	219.8	356.5	99.63	0.30
Nanocomposite	500 °C	230.7	360.2	96.70	3.30
Nanocomposite	650 °C	230.1	361.3	98.50	1.05
Nanocomposite	850 °C	230.3	362.8	99.98	0.07

TEM micrographs in Fig.3 visualize the content of the residue ash after combustion at the three temperatures, in air atmosphere. As seen in the first column (Fig 3a), at 500^{o}C the residue ash (3.3%) is completely composed of unburned single MWCNTs and GNPs, or their loose agglomerates. At 650 ^{o}C (Fig. 3b), the residue decreases to 1.5% and consists mostly of single airborne particles, MWCNTs and GNP and some soot nanoparticles of primary sizes of 10–30 nm. The nanotubes are of about 30 nm in diameter and few microns in length that are very similar to the original MWCNT size. Similar finding is observed for the GNP particles. While, at 850 ^{o}C (Fig. 3c), the amount of the residue ash strongly decreases to 0.07%, confirming that the carbonaceous fillers are mostly degraded. Indeed, the MWCNTs are missing in the residue ach, but unexpected content of GNP particles is observed and they are mainly displayed as fractal aggregates mixed with some soot nanoparticles.

The observations reveal that large amounts of single isolated airborne MWCNTs (<50 nm diameter and >1 µm length) and GNPs (>100 nm), as well as their loose fractals (1-2 µm) can be released during burning in air atmosphere, addressing therefore a new kind of safety issues with regard to the combustion/incineration of nanowastes or accidental fires. The airborne particles of GNPs and MWCNTs may either stay in the char residues, or may be released in the gas phase during incineration or fire. Their fate depends of local operating conditions of the burning process.

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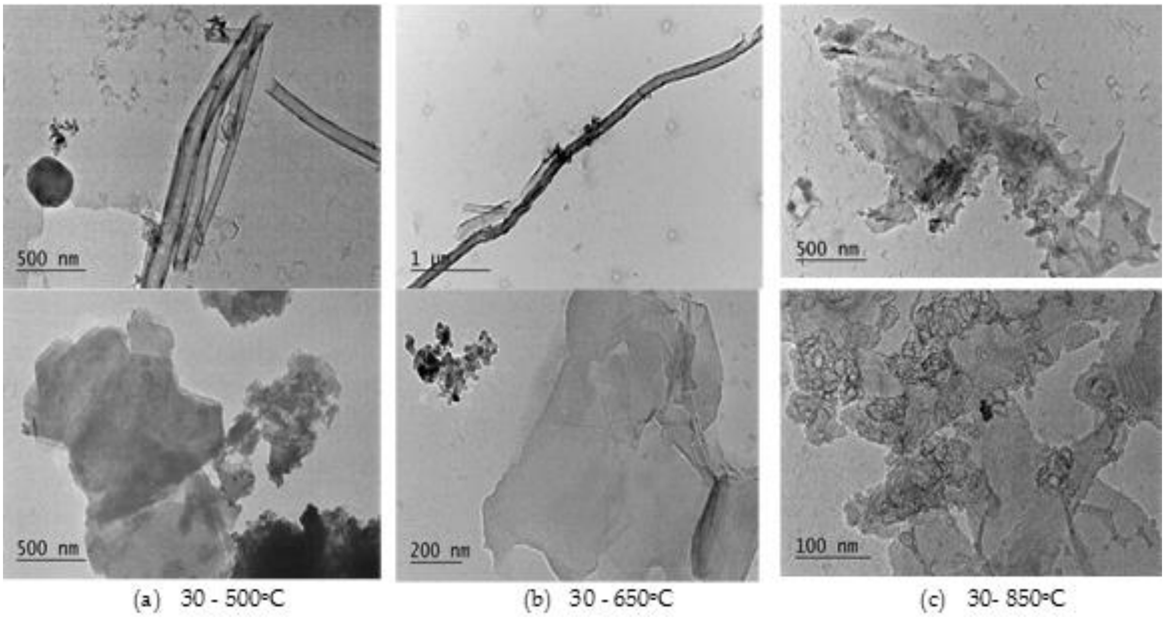

(a) 30 - 500ºC (b) 30 - 650ºC (c) 30- 850ºC

Fig.3. TEM micrographs of MWCNTs (first line) and GNPs (second line) observed in the residue ash at the three decomposition temperatures: (a) 500 ºC, (b) 650 ºC and (c) 850ºC in air atmosphere

3.3. Risk assessment associated with end-of life of nanocomposite food packaging materials

Risk could be defined as a combination of the probability of occurrence of an event and its consequences, establishing a negative outcome. The methodology we applied to analyze and quantify the risk is borrowed from standards and guidelines presented in several regulatory documents, such as: Risk Management Standard ISO 31000: 2009 [35], British Standard BSI 2007 on safe handling and disposal of manufactured nanomaterials [36], USEPA Guidelines for Ecological Risk Assessment [37], and the British CSIRO Safe Handling and Use of Carbon Nanotubes [38]. In this study, the risk is mainly defined according to standard ISO 31000: 2009 [35] as a comprehensive process of analysis and categorization, where the risk could be assessed quantitatively or qualitatively, depending on the probability of occurrence of the possible consequences.

To quantify the risk (R) of the release of MWCNTs and GNP from 3 wt% GNP/MWCNT/PLA film at the end-of-life, as food packaging wastes, we have adopted the three factors method (C.E.L.), i.e. grading the three risk analysis factors: Consequences (C), Exposure (E), and Probability/Likelihood (L). The C.E.L. model is widely recognized method of analysis and quantitative risk assessment [39,40]. Therefore, we have applied it for risk assessment in four most popular scenarios for treatment of the food packaging wastes: biodegradation, combustion, burning in open air and accident fire. The risk analysis factors are defined according to C.E.L. model [39], as follows:

- Consequences (C) represent the undesired results of an event or series of events. In this work, consequences are determined from the amount of the released MWCNTs and GNPs, as graded according to the recommended exposure limit of Carbon Nanotubes and Nanofibers (μg) in air (1 m^3), REL=1μg/m^3, proposed by NIOSH [41]. The NIOSH REL is expected to reduce the risk for pulmonary inflammation and fibrosis. Thus, six grades from 1 to 100 [39] are used for quantification of consequences (xREL = 1 to > 1 000 000), as shown in Table 2.

- Exposure (E) shows how often a certain danger can occur, how much the system is often threatened by accidents. The exposure estimates are based on the E-classification method [39], with six steps in the range from 0.5 to 1 (Table 2).

- Likelihood (L) shows how likely it is to have consequences. The following six steps of grades from 0.5-10 are used to quantify this factor, as shown in Table 2.

- The risk (R) is defined as the quantity comprised of the product of the three parameters: consequences (C), exposure (E) and probability (L): R = C x E x L. The eligibility of risk to health and environment is classified in the following five risk areas presented in Table 2, namely: minimal,

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acceptable, high, very high and unacceptable (hazard), depending on the calculated values of risk (R) varying from < 20 to > 400 [39]. The end-results of the risk assessment determine the eligibility of the identified risk and the need to apply measures to prevent or limit it.

Table 2. The grades for Consequences (C), Exposure (E), Likelihood (L) and Risk (R) used in this study

Consequences (C)	**Exposure (E)**	**Likelihood (L)**	**Risk (R)**
1 = minimal (≤ 100 REL)	0.5 = very rare (less than once a year)	0.2 = not imagine at all	< 20 = minimal
3 = significant (100 -1000 REL)	1 = rarely (once a year)	0.5 = almost impossible	20 - 70 = acceptable
7 = serious (1000 - 10 000 REL)	2 = sometimes (once a month)	1 = unbelievable, but long-term still possible	70 – 200 = high
15 = very serious (10 000 - 100 000 REL)	3 = happening (once a week)	3 = not be normal, but possible	200 - 400 = very high
40 = major damage (100 000 - 1 000 000 REL)	6 = regular (daily)	6 = completely possible	> 400 unacceptable (hazard)
100 = crash (>> 1 000 000 REL)	10 = continuous	10 = almost certain	

3.3.1. Quantitative and qualitative risk assessment for the release of GNP and MWCNTs

For the quantitative risk assessment, we have used data obtained above for the release of GNP and MWCNTs from 3 wt% GNP/MWCNT/PLA film, during the degradation at ultra-strong dynamic test, as well as the burning at three heating temperatures 500, 650 and 850°C in air atmosphere. Importantly, for the biodegradation (i.e. composting, weathering), we have assumed that the total amount of 3 wt% GNPs/MWCNTs nanofiler may release from the GNP/MWCNT/PLA nanocomposite film in form of agglomerates and single nanoparticles due to the full degradation (hydrolysis) of the PLA polymer. While for burning processes, like: combustion, burning in open air and accident fire, the released GNPs and MWCNTs will depend from the heating temperature. The results from thermogravimetric analysis in Table 1 are used to simulate the combustion at 500, 650 and 850°C in air atmosphere. For analysis of risk to human end environment, the released GNPs and MWCNTs are estimated for 100 kg wastes. Moreover, we have assumed that the single airborne nanoparticles of GNPs and MWCNTs (≤100 nm), that may release in 1m^3 air or soil are only 1% of the total amount of released nanoparticle agglomerates during the four scenarios studied.

Table 3. Risk assessment by CEL model for the release of GNPs and MWCNTs from 3% GNP/MWCNT/PLA film during biodegradation, combustion, burning and accident fire.

Scenario	**Amount of nano wastes [kg]**	**Released total amount GNP/ MWCNT [kg]**	**Released GNP/MWCNT nanoparticles in 1 m^3 air [μg/m^3]**	**Conse-quences (C) [x REL]**	**Exposure (E)**	**Likelihood (L)**	**Risk, (R) = C x E x L**
Biodegra-dation	100	3	30 000	15	3	6	270 very high
Combustion 850 – 650 – 500°C	100	0.07 – 1.05 – 3.3	70 – 10 500 – 33 000	1 - 15	10	10	100-1500 high - to - hazard
Burning of wastes at 500°C	100	3.3	33 000	15	2	6	180 high
Accident fire 500°C	100	3.3	33 000	15	0.5	3	22.5 acceptable

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The admissibility of the human and environmental risk is presented as a multiplication of the three factors (R = C x E x L). The Table 3 presents the three risk analysis factors and the quantitative risk assessment for the four scenarios: biodegradation; combustion at 500, 650 and 850°C; burning in open air (at 500°C) and accident fire (at 500°C). As seen, the risk of GNPs and MWCNTs from the biodegradation is of R=270, while the risk from combustion vary within R= 100 – 1500 depending on the heating temperature (500-850°C). However, the risk from burning of wastes in open air (in landfills) is quite high (R=180), while this from accident fire is low of R=22.5, due to the very rare exposure.

For the qualitative risk assessment, we used the approach described by Aven [40], which represents the dependence of the "consequences" in a function to the "frequency" of occurrence, the last being a derivative of "exposure" and "likelihood". This dependence is showed in Fig. 4, for the purpose of classification of the risk of MWCNTs and GNP release from 100 kg of 3 wt% PLA/MWCNT/GNP nanocomposite wastes, under the scenarios of biodegradation, combustion (500-850°C), burning in open air (at 500°C) and accident fire (at 500°C).

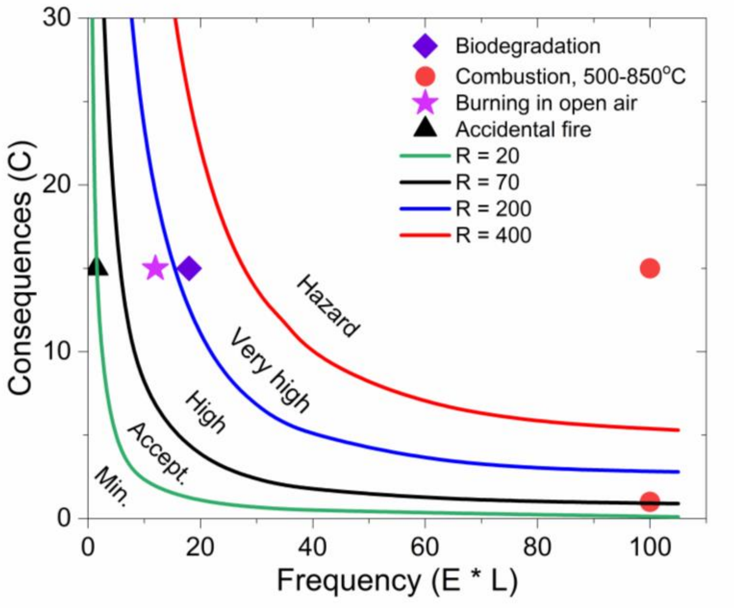

Fig. 4. Qualitative risk assessment: consequences vs. frequency of occurrence of GNP and MWCNT exposure, related to four scenarios of the end-of life of 3wt% GNP/MWCNT/PLA packaging films: biodegradation, combustion, burning and accident fire. Risk is estimated for 100 kg nanocomposite wastes.

The lines represent the "constant risk" at the following levels of risk: R = 20, R = 70, R = 200 and R = 400, and outline the five risk zones: minimum (R <20); acceptable (20 <R <70); high (70 <R <200); very high (200 <R <400) and hazard (R> 400). The experimental points represent the risk of exposure to MWCNTs and GNPs from the PLA nanocomposite film throughout the four scenarios of the waste treatment, listed in Table 3.

As shown on Fig. 4, the scenario of total biodegradation of GNP/MWCNT/PLA nanowastes leads to “very high” risk for release of GNPs and MWCNTs nanoparticles to the environment. This may pose questions associated with environmental and human risks due to local composting of post-consumer wastes, when those nanoparticles enter the soil.

Combustion of nanowastes at heating temperatures of 500°C may result in “unacceptable risk/hazard” from airborne GNPs and MWCNTs, however by increasing the heating temperature to 850°C the risk decreases to “high”. Particularly, burning of nanowastes in open air (e.g. in landfills), that is a regular practice in underdeveloped regions, is resulted in “high” risk. Therefore, such practice must be addressed and limited by the regulators, as it may affect more people and cause significant damage to the environment in those regions. The scenario of accident fire lead to “acceptable” risk, but it will have a local negative effect therefore preventive measures for safety have to be taken into account.

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3.4. *Safety concerns*

Studies comparing the graphene nanoplates, GNPs and carbon nanotubes, CNTs are very rare, making it difficult to analyze their overall safety and risk [42]. In general, authors agree, that despite their common carbon structure, CNTs and GNPs are two very different nanomaterials, due to their different physical and chemical characteristics. Dimensions, surface chemistry and impurities are equally important for determining the aggregation, degradation and toxicological effects of CNTs and GNPs. Their shape (tubular vs. plane) and their dimensions (2D vs. 1D) are key structural differences. The CNTs tend to form entangled aggregates, and GNPs tend to stack in several layers. GNPs are characterized by a lower aspect ratio (length/width), greater surface area and better dispersion in most solvents, compared to CNTs. The colloidal dispersions of graphene can be obtained without metallic impurities, with high stability and less aggregation. All those characteristics could theoretically offer significant advantages of GNPs over CNTs, in terms of risk management and safety.

Our current study expands the upper safety concerns comparing GNPs and CNTs, by finding that large graphene nanosheets indeed release from PLA based nanocomposite films at temperatures above the glass transition, during ultra-strong dynamic migration test. While MWCNTs remain embedded in the polymer matrix, if the PLA matrix is partly degraded. Moreover, GNPs and MWCNTs are found remaining unburned in the residue after combustion up to 650^{o}C, while at 850^{o}C only GNPs and carbon soot are found, but not MWCNTs.

In this research, we stress on safety concerns at the end-of-life of nanocomposite food packaging, related to different waste treatment, such as: biodegradation, combustion, burning in open air and accident fire. Safety concerns may arise due to biodegradation and composting of nanowastes based on biodegradable polymers. Composting has the potential to transfer biodegradable plastics into useful soil amendment products by an accelerated degradation. However, special care should be taken while handling local composting of biodegradable nanowastes to limit potential environmental risks due to release of nanoparticles in the soil from the compost. The risks and fate of GNP and CNT nanoparticles in ground water and air is needed of further research in the biodegradation scenario of nanowastes. Safety information for prevention of risks is presently lacking in the Material data sheet, though very important to safety assessment. Moreover, specific labeling for prevention from composting of wastes could be adopted as safety measures for some nanocomposite food packaging.

Combustion of nanocomposite wastes to produce energy is recently discussed as a nanowaste management strategy, thus the risks for nanoparticle emission during incineration of thermoplastic nanocomposites must be addressed and investigated. Our current study confirm that the combustion of PLA-based nanocomposites could form residues ashes containing unburned GNPs and MWCNTs, this associated with "hazard" to "high risk", depending on the temperature. The amount of unburned nanoparticles may be controlled by increasing the heating temperature above 500 - 850^{o}C, however, single GNPs and MWCNTs may also release in the combustion gas phase. Such release can be a source of risk in accidental scenarios, like fire, uncontrolled incineration/combustion, or absence of nano-filtration of the combustion gas phase. Regulatory limitations imposing the control on the combustion processes and exhaust gases will contribute to safety and risk prevention.

Safety concerns arise about common practice in some regions for burning of nanowastes in open air, e.g. in landfills or single-use disposable systems, due to the gradual increase of nanowastes from food packaging. As shown in this study, such regular practice leads to "high" risk for human and environment from airborne nanoparticles, such as GNPs and MWCNTs. Regulatory measures imposing the limitation of burning of nanowastes in open air are still missing

4. Conclusions

The release of graphene nanoplatelets and multiwall carbon nanotubes from polylactic based film at the end-of-life of wastes treatment was investigated during degradation and combustion/burning. The released airborne nanoparticles and the degradation of the nanocomposte film during ultra-strong dynamic migration test were confirmed by different visualization methods (TEM, AFM, SEM). Thermogravimetric analysis in air atmosphere was used to simulate the combustion of nanocomposite wastes. It was found that, single graphene nanoplatelets of nanosized thickness and

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length of 100-1000 nm, as well as their micron size loose aggregates indeed release in relatively large amounts from the PLA nanocomposite film at high temperature dynamic treatment due to partial degradation of the PLA polymer. While, the release of the entangled MWSNTs is possible only after full degradation (hydrolysis) of the PLA matrix polymer.

Combustion or burning at 500 and 650 °C result in residue ash, which contains mainly single airborne GNPs and MWCNTs, while at 850°C the small amount of residue ash (~0.07%) contains only GNPs and amorphous carbon soot. Therefore, the MWCNTs fully degrade at the heating temperature of 850°C, while the GNPs are still remaining in the residue.

This information is used to assess the risks at the end-of-life of nanowastes, by adopting a 3-factors, C.E.L. model. In this work, consequences (C) were determined from the amount of the released MWCNTs and GNPs as graded according to the recommended exposure limit of carbon nanotubes, REL=1μg/m^3, proposed by NIOSH. The exposure (E) and likelihood (L) were estimated based on the E-classification method. Hence, new concerns with the end-of-life nanostructured materials were emerged. The biodegradation of nanowastes, as well as the treatment of nanowastes by combustion and burning in open air, at low temperatures of 500°C, lead to a "very high", hazard" and "high" risk, respectively. Such treatment of nanowastes may pose a potential release of GNPs and MWCNTs into the environment, with all associated environmental and human risks, that are presently not accounted for. Appropriate safety measures were discussed for the end-of-life phase of nanowastes in order to avoid or prevent the risks.

Author Contributions:
In this study, the concept, methodology, analysis of results and writing of manuscript were performed by S.K.; The AFM visualization was conducted by E.I.; The methodology and manuscript text were examined by N.V. and E.I. All authors read and approved the final manuscript.

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References

1. De Azeredo, H.; Mattoso, L.H.C.; McHugh T.H. Nanocomposites in Food Packaging–A Review. In: *Advances in Diverse Industrial Applications of Nanocomposites*. Reddy, B. Ed.; Intech Open Science, 2011; Ch. 4, pp. 57-78; ISBN: 978-953-307-202-9
2. Silvestre, C.; Pezzuto, M.; Cimmino, S.; Duraccio, D. Polymer Nanomaterials for Food Packaging: Current Issues and Future Trends. In Book: Ecosustainable Polymer Nanomaterials for Food Packaging: Innovative Solutions, Characterization Needs, Safety and Environmental Issues; 1st ed.; Silvestre, C; Cimmino, S., Eds.; CRC Press Taylor & Francis Group, US, 2013, pp. 2-28, ISBN 9781138034266
3. Chandhry, Q.; Scotter, M.; Blackburn, J.; Ross, B.; Boxall, A.; Castle, l. Applications and implications of nanotechnologies for the food sector. *Food Additives and Contaminants*, **2008**, *25*, 3, 241-258, https://doi:10.1080/02652030701744538
4. Randviir, E.P.; Brownson, D.A.C.; Banks, C.E. A decade of graphene research: production, applications and outlook. *Materials Today* **2014,** *17*, 9, 426-432, https://doi:10.1016/j.mattod.2014.06.001
5. Honarvar, Z.; Hadian, Z.; Mashayekh, M. Nanocomposites in food packaging applications and their risk assessment for health. *Electronic Physician*, **2016**; *8*, 6, 2531-2538, https://doi:10.19082/2531
6. Wu, L.L; Wang, J.; He, X.; Zhang, T.; Sun, H. Using graphene oxide to enhance the barrier properties of poly(lactic acid) film. *Packaging Technol Sci*. **2014**; *27*, 693–700, https://doi.org/10.1002/pts.2058
7. Du, J.; Cheng, H.M. The fabrication, properties, and uses of graphene/polymer composites. *Macromol Chem Phys*. **2012**; *213*, 1060–1077, https://doi.org/10.1002/macp.201200029
8. Cui, Y.; Kundalwal, S.I.; Kumara, S. Gas barrier performance of graphene/polymer nano-composites. *Carbon* **2016**; *98*, 313–333, DOI: https://doi.org/10.1016/j.carbon.2015.11.018
9. Ivanov, E.; Kotsilkova, R. Reinforcement effects of carbon nanotubes in polypropylene: rheology, structure, thermal stability, nano- micro- and macro mechanical properties. In: Handbook of nanoceramic and

Peer-reviewed version available at *Materials* **2018**, *11*, 2346; doi:10.3390/ma11122346

nanocomposite coatings and materials, Makhlouf, A; Scharnweber, D. Eds., Elsevier, Ch.17, **2015**, pp. 351–383, ISBN: 978-0-12-799947-0.

10. Kotsilkova, R.; Ivanov, E.; Krusteva, E.; Silvestre, C.; Cimmino, S.; Duraccio, D. Evolution of rheology, structure and properties around the rheological flocculation and percolation thresholds in polymer nanocomposites. In Book: Ecosustainable Polymer Nanomaterials for Food Packaging: Innovative Solutions, Characterization Needs, Safety and Environmental Issues; 1st ed.; Silvestre, C.; Cimmino, S Eds.; CRC Press Taylor & Francis Group, US, Ch.3**, 2013**, pp. 55-86, ISBN 9781138034266
11. Novack, B.; Ranville, J.F.; Nowack, S.; David, R.M.; Fissan, H.; Morris, H.; Shatkin, J.A.; Stintz, M.; Zepp, R.; Brouwer, D. Potential release scenarios for carbon nanotubes used in composites, *Environ Int., 2013*; *59*, 1-11, DOI:10.1016/j.envint.2013.04.003
12 Arvidsson, R.; Molander, S.; Sanden, B.A.. Review of potential environmental and health risk of nanomaterial graphene. *Human Ecological Risk Assessm*. **2013**; *19*, 4, 873-887. https://doi.org/10.1080/10807039.2012.702039
13 Lowry, G.V.; Gergory, K.B.; Apte, S.C.; Lead, J.R. Transformation of nanomaterials in the environment", *Environmental Sci. Tech*. **2012**; *46*, 6893-6899, https://doi.org/10.1021/es300839e
14. Kingston, C.; Zepp, R.; Andrady, A.; Boverhof, D.; Fehir, R.; Hawkins, D.; Roberts, J.; Sayre, P.; Shelton, B.; Sultan, Y.; Vejins, V.; Wohlleben, W. Release Characteristics of Selected Carbon Nanotube Polymer Composites. *Carbon* **2014**, *68*, 33–57, http://dx.doi.org/10.1016/j.carbon.2013.11.042
15. Harper, S.; Wohlleben, W.; Doa, M.; Nowack, B.; Clancy, S.; Canady, R.; Maynard, A. Measuring Nanomaterial Release from Carbon Nanotube Composites: Review of the State of the Science. *Journal of Physics: Conference Series* **2015**, *617*, 012026, http://dx.doi.org/10.1088/1742-6596/617/1/012026
16. Schlagenhauf, L.; Nuesch, F.; Wang, J. Release of Carbon Nanotubes from Polymer Nanocomposites (Review). *Fibers* **2014**, *2*, 108-127; http://dx.doi.org/10.3390/fib2020108
17. Petersen, E.J.; Zhang, L.; Mattison. N.T. Potential release pathways, environmental fate, and ecological risks of carbon nanotubes. *Environ. Sci. Technol*. **2011**, *45*, 9837–9856, http://dx.doi.org/10.1021/es201579y
18. Duncan, T.V.; Pillai, K. Release of engineered nanomaterials from polymer nanocomposites: diffusion, dissolution, and desorption. *ACS Appl Mater Interfaces*. **2015**; *7*, 2–19, http://dx.doi.org/10.1021/am5062745
19. Velichkova, H.; Petrova, I.; Kotsilkov, S.; Ivanov, E.; Vitanov, N.K.; Kotsilkova, R. Influence of Polymer Swelling and Dissolution in Food Simulants on the Release of Graphene Nanoplates and Carbon Nanotubes from Poly(lactic) acid and Polypropylene Composite Films. *J. Appl. Polym. Sci*. **2017**; *134*, 44, 45469, http://dx.doi.org/10.1002/app.45469
20. Velichkova, H.; Kotsilkov, S.; Ivanov, E.; Kotsilkova, R.; Gyoshev, S.; Stoimenov, N.; Vitanov, N.K.. Release of carbon nanoparticles of different size and shape from nanocomposite poly(lactic) acid film into food simulants. *Food Additives & Contaminants: Part A*, **2017**; *34*, 6, 1072-1085, http://dx.doi.org/10.1080/19440049.2017.1310396.
21. Kotsilkov, S.; Ivanov, E.; Vitanov, N.K. Study on the release of graphene and carbon nanotubes at the end-of-life phase of polymer nanocomposites: risk assessment and safety concerns. In. Proceedings of ISER 144th International Conference, New Delhi, India, 15th-16th July 2018, ISBN 978-93-88192-19-4
22. Bernard, C.; Nguyen, T.; Pellegrin, B.; Holbrook, R.D.; Zhao, M.; Chin, J. Fate of graphene in polymer nanocomposite exposed to UV radiation, *Journal of Physics: Conference Series*, **2011**, 304, 012063, https://doi.org/10.1088/1742-6596/304/1/012063
23. Musee, N. Nanowastes and the environment: potential new waste management paradigm. *Environ Int*. **2011**; 37, 1, 112–128, https://doi.org/10.1016/j.envint.2010.08.005
24. Mueller, N.C.; Buha, J.; Wang, J.; Ulrich, A.; Nowack, B. Modeling the flows of engineered nanomaterials during waste handling. Environ. Sci. Process. Impacts 2013, 15, 251–259, DOI:
25. Bouillard, J.; R'Mili, B.; Moranviller, D.; Vignes, A.; Le Bihan, O.; Ustache, A.; Bomfim, J.S.; Frejafon, E.; Fleury, D. Nanosafety by design: risks from nanocomposite/nanowaste combustion. *J. Nanoparticle Res*. **2013**, 15, 1–11, http://dx.doi.org/10.1007/s11051-013-1519-3
26. Song, J.H.; Murphy, R.J.; Narayan, R.; Davies, G. B. H. Biodegradable and compostable alternatives to conventional plastics. *Philos Trans R Soc Lond B Biol Sci*. **2009**; *364*, 1526, 2127–2139, DOI:10.1098/rstb.2008.0289
27. Narayan, R. Rationale, drivers, standards, and technology for biobased materials. In the book: Renewable resources and renewable energy, Graziani, M.; Fornasiero, P. Eds; Boca Raton, FL: CRC Press, Taylor & Francis Group, Part 1, 2006, ISBN 9781138198524

28. European Commission Regulation. (EU) No. 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. *Off J EU*. **2011**; L 12:1–89, http://data.europa.eu/eli/reg/2011/10/oj
29. Mutsuga, M.; Kawamura, Y.; Tanamoto, K. Migration of lactic acid, lactide and oligomers from polylactide foodcontact materials. *Food Addit Contam Part A*. **2008**; *25*, 1283–1290, https://doi.org/10.1080/02652030802017529
30. Xu, Q.; Yin, X.; Wang, M.; Wang, H.; Zhang, N.; Shen, Y.; Xu, S.; Zhang, L.; Gu, Z. Analysis of phthalate migration from plastic containers to packaged cooking oil and mineral water. *J Agric Food Chem*. **2010**; *58*, 11311–11317, DOI:10.1021/jf102821h
31. Ebnesajjad, S. Plastic Films in Food Packaging: Materials, Technology and Applications. A Survey of Regulatory Aspects of Food Packaging, PDL Handbook Series, Elsevier. 2013; Volume 16, pp. 345-388, ISBN: 9781455731121
32. Nyden, M.R.; Harris, R.H.; Kim, Y.S.; Davis, R.D.; Marsh, N.D.; Zammarano, M. Characterizing particle emissions from burning polymer nanocomposites. Nanotechnology: Advanced Materials, CNTs, Particles, Films and Composites - Technical Proceedings of the NSTI Nanotechnology Conference and Expo, NSTI-Nanotech 2010, Volume 1, pp 717–719, ISBN 9781439834015.
33. Li, J.; Tong, L.; Fang, Z.; Gu, A.; Xu, Z. Thermal degradation behavior of multi-walled carbon nanotubes/polyamide 6 composites. *Polym. Degrad .Stab*. **2006**; *91*, 2046–2052, https://doi.org/10.1016/j.polymdegradstab.2006.02.001
34. Yang, S.; Castilleja, J.R.; Barrera, E.V.; Lozano, K. Thermal analysis of an acrylonitrile–butadiene–styrene/SWNT composite. *Polym. Degrad. Stab*. **2004**; *83*, 383–388, DOI: 10.1016/j.polymdegradstab.2003.08.002
35. ISO Guide 73:2009 / ISO 31000:2009 Risk management - Principles and guidelines, 2009, https://www.iso.org/standard/44651.html
36. BSI (British Standard) PD 6699-2:2007. Nanotechnologies – Part 2: Guide to safe handling and disposal of manufactured nanomaterials, 2007, ISBN 978 0 580 60832 2
37. USEPA (US Environmental Protection Agency). Guidelines for Ecological Risk Assessment. Washington, DC, USA, 1998, EPA/630/R-95/002F
38. CSIRO (Commonwealth Scientific and Industrial Research Organisation). Safe Handling and Use of Carbon Nanotubes, Safe Work Australia, (ed. Haywood G.) 2011, ISBN 978-0-642-33351-3
39. Vitanov, N.K.; Dimitrova, Z.I. Risk analysis. Technological, political and other risks. Qualitative analysis of risk, Publishing House "Vanio Nedkov", Volume 1, 2015, ISBN:978 -619 -194 -00.
40. Aven,T.; Renn, O. Risk management and governance. Concepts, guidelines and applications. Springer, Volume 16, 2010, ISBN 978-3-642-13926-0.
41. NIOSH (National Institute of Occupational Safety and Health). Current Intelligence Bulletin 65: Occupational Exposure to Carbon Nanotubes and Nanofibers. Publication No. 2013–145, April 2013, https://www.cdc.gov/niosh/docs/2013-145/default.html
42. Bussy, C.; Ali-Boucetta, H.; Kostarelos, K. Safety considerations for graphene: lessons learnt from carbon nanotubes. *Accounts of Chemical Research*, **2013**; *46*, 3, 692–701, https://pubs.acs.org/doi/10.1021/ar300199e