

# New Insights into Marine Pollution by Nanoplastics: Chemical, Ecological, Health, and Occupational Safety Perspectives

Howida A. Fetouh<sup>1</sup>, Taher S. Kassem<sup>1</sup>, Salam N. Hattawi<sup>2</sup>, Reem A. ElTatawy<sup>1,\*</sup>, Mai S. Alsubaie<sup>1</sup>, Ahmed M. Abed<sup>3</sup>, Ahmed S. Tawfeek<sup>4</sup>, Jihad M. El Desouky<sup>5</sup>, Shahenaz M. Abd\_Ellah<sup>6</sup>

<sup>1</sup>Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

<sup>2</sup>Northern technical university, college of health and medical techniques, Department of renal dialysis techniques, Kirkuk, Iraq.

<sup>3</sup>Geology Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

<sup>4</sup>El-Alameen Hospital, Alexandria University, Egypt.

<sup>5</sup>Clinical Pathology Department, Faculty of Medicine, Alexandria University, Egypt.

<sup>6</sup>Department of Biological & Geological Science, Faculty of Education, Alexandria University, Egypt.

\* Correspondence Address:

Reem A. ElTatawy: Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.  
Email: Reem.Amgad@alexu.edu.eg.

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**ABSTRACT:** This review provides an up-to-date and comprehensive examination of nanoplastics (NPs), focusing on the chemistry aspect, widespread pollution, and the associated health risks arising from the discharge of non-biodegradable NPs into the marine environment. By analyzing previous studies, the need to understand the fate, degradation, fragmentation, transport, and cytotoxicity of NPs is highlighted. While scientists have made significant efforts to investigate the mitigation of plastic pollution, the research on NPs remains limited. This review aims to contribute to the understanding of the key sources of NPs pollution as well as the hazards that impact the marine environment and consequently human health. The review discusses the details of the advanced awareness efforts, including management, monitoring, and regulatory measures against NPs pollution. The most hazardous pollution sources are mills in the rubber and plastics industries, deterioration, and plastic flammability. It also emphasizes the urgent need for continued research and action to address the challenges posed by NPs pollution.

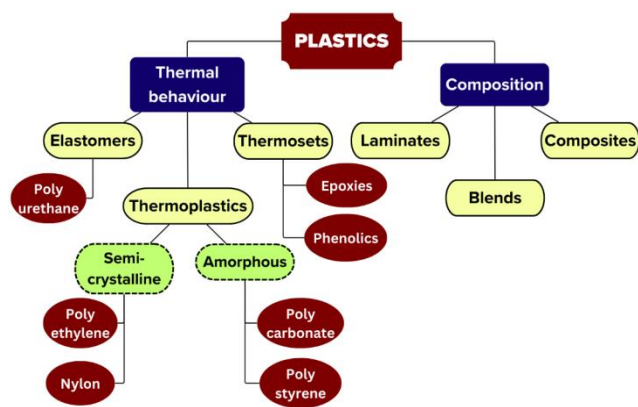
## 1. INTRODUCTION

In recent years, global marine ecosystems have faced a significant decline in fish production due to increasing pollution caused by microplastics (MPs) and NPs. These pollutants adversely affect water quality, sediments, and aquatic biota [1]. To mitigate NPs pollution and restore fish stocks, government institutions have implemented various strategies. However, long-term studies on the ecological and human health impacts of NPs remain insufficient. Addressing the issue of NP pollution necessitates a detailed understanding of several related topics, as outlined below.

### 1.1. Chemistry of Nanoplastics

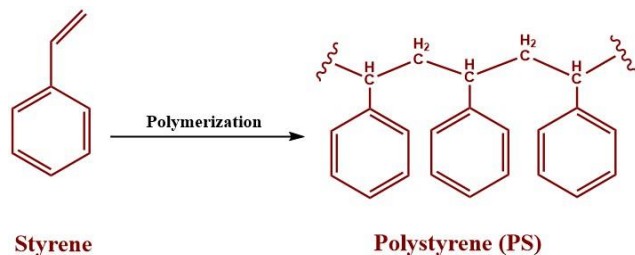
Synthetic plastics produce a huge range of performance attributes due to their wide variety. Plastics are ever-present in

modern life: electrical insulation, pipelines, consumer goods, construction, and diverse applications. Plastics are classified based on thermal behavior and composition into (elastomers, thermoplastics, and thermosets) or (laminates, blends, and composites), respectively, as shown in **Figure 1**. Thermoplastics, which include amorphous and semi-crystalline polymers, soften and melt upon heating and are reshaped multiple times *via* casting and solidification on cooling. Common plastics include polypropylene (PP), low- and high-density polyethylene (LDPE, HDPE), polyvinyl chloride (PVC), polyurethane (PU), polyethylene terephthalate (PET), polystyrene (PS), and polyamide (PA) [2].



**Figure 1.** Classification of plastics based on thermal response (to heat) and composition.

Industrial plastics are produced through a chemical polymerization process. Monomers in a liquid or gaseous state react to form long-chain polymers [1]. For example, PS used in Styrofoam coffee cups is synthesized by polymerizing styrene monomers into a solid form, as shown in Figure 2 [2, 3].



**Figure 2.** Polymerization reaction of styrene monomer. PS is a tasteless, odorless, and non-toxic versatile thermoplastic polymer characterized by a glassy solid state at room temperature.

The wastes of expanded or extruded foamed PS are spontaneously fragmented and dispersed in the environment. The mobilized chemical additives are a challenge. Photolytically degraded foamed PS consumed by rafting organisms and marine animals are exposed to elevated concentrations of natural and anthropogenic surface-active chemicals. Fragmentation is accentuated by milling in the swash zone and abrasion at beaches. Wind assisted the transport [3].

Heating above the glass transition temperature ( $T_g$ ), PS becomes pliable, allowing molding, extrusion, and solidifying by cooling. PS is applied in electrical insulation, packaging, disposable cutlery, hybrid anticorrosive protective coating, medical devices, and parts of refrigerators and air conditioners due to their mechanical strength, durability, and thermal insulation [4, 5]. Despite these benefits, PS is non-biodegradable and persists in the environment for hundreds of years, causing significant environmental damage upon accumulation. PS pollution is visually identified by yellow discoloration [6, 7].

PS resists chemicals such as weak acids, alcohols, oils, greases, and waxes. However, it dissolves in chlorinated solvents (such as dichloromethane and chloroform), benzene, and toluene [8]. PS softens by heating, melts at 240°C, and thermally decomposes at 270°C. Aging and prolonged use

alter its chemical reactivity [9]. Recycling PS wastes through biodegradation by microorganisms or enzymatic hydrolysis is an essential strategy for maintaining environmental sustainability [10]. Blending with polyvinyl alcohol under controlled mechanical conditions enhances its properties such as tensile strength, elongation at break, and electrical resistivity [11]. The PS blend material demonstrates excellent thermal stability, as indicated by high  $T_g$ , softening temperature, and  $T_D$ , along with minimal weight loss during thermal degradation [12].

Silicon rubber is a flexible and malleable plastic that can be designed in diverse shapes and surfaces. It is often used in radiation shields, medical imaging equipment for full protection against gear, shields for thoracic computed tomography radiation scans, light weight (aerospace and soldering), durable by thermal and chemical stability due to the strong Si-O bonds [13, 14]. PVC (transparent low crystalline plastic) is the most frequently produced synthetic thermoplastic polymer and has the largest production after polyethylene and polypropylene. Because of its versatility, availability, and low cost, it is favored for electrical wires' insulation. High  $Cl_2$  content increased flame resistance represented in fair heat deflection temperature. Stabilizer additives delay and retard the thermal- and photo degradation; resist alcohols, mild acids, bases, and salts, but are attacked by ketones, halogenated solvents, aldehydes, phenols, esters, and ethers. Plasticizers improve flexibility for wide applications in wire covering and shoe soles [15].

The unplasticized PVC is a hard plastic, commonly used in pipes and window profiles. Due to its durability and low cost, it is used in many advantageous applications, especially in construction, insulating covers for the electrical cables, window frames, and house siding. PVC failed in grades different than polyolefin, which ranked favorably in terms of green chemistry and recyclability in the life cycle assessment [15]. In the US, its production during the time period 2000-2009 declined due to negative environmental impact, while polyolefin production increased. PVC applications are limited by its low thermal stability, impact strength, and brittleness. Phthalated plasticizers have raised certain public concerns about health matters due to toxins associated with the burning of PVC and its vinyl chloride monomer. This disadvantage reduced PVC use in more personal applications over the years. Its composites containing reinforcing fillers such as calcium silicate, black carbon, Kevlar, glass fibers, and mica have better properties. For example, the use of mica improved the physical, mechanical, and electrical properties; decreased thermal expansion, increased stiffness, and decreased abrasion and wear to the processing apparatus [16]. PVC is polymerized as follows: refining crude oil or natural gas gives ethane (cracking gives ethylene), which is converted by  $Cl_{2(g)}$ , from NaCl electrolysis, to ethylene dichloride, which is then cracked to create HCl and vinyl chloride monomer. Another preparation method involves ethane chlorination using  $FeCl_3$  as a catalyst, giving 1, 2-dichloroethane, which is annealed at 650 °C and converted into Cl-ethane (vinyl chloride monomer) that is polymerized into PVC using a catalyst under high pressure [17].

The core PVC formulation slowly sparked growing concerns over decades of use. Although PVC is inert and stable, its monomer is carcinogenic and toxic, and monitored and controlled carefully in the soil using (VMC sensors) sealed

Philips Petroleum Co. Release dry HCl cured to prevent conversion to HCl. Recent environmental concerns required monitoring of chlorinated dioxin to be eliminated from PVC production companies. In 2011, the Environmental Protection Agency (EPA) suggested an emissions standard for the US PVC production facilities, restricting the reduction as possible of these production facilities from wastewater, equipment leaks, storage vessels, heat exchangers, and process vents [18].

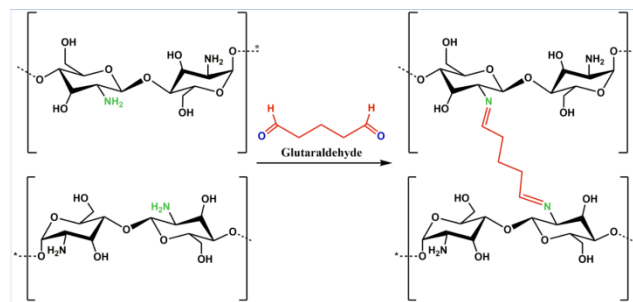
The compounding of cheap PVC into a useful processable material produced MPs and NPs. Non-plasticized PVC is utilized for pipes and construction materials. Certain types of additives facilitate extrusion or compression molding into micro beads or sheets in composites preparation. For flexibility and softness, above 30 Wt. % plasticizers are added. Examples are phthalate-based compounds that partially leach and disrupt the mammalian endocrine systems. This issue differs according to phthalate type. High molecular weight (Mw.) phthalates have low risk, such as Diisononyl phthalate (DINP), Diisodecyl phthalate (DIDP), and Dipropylheptyl phthalate (DPHP); so, they are used in wall covering, furniture, and floors. The low Mw. phthalates such as Diethylhexyl phthalate (DEHP), Dibutyl phthalate (DBP), and Butyl benzyl phthalate (BBP) have been constrained and eliminated by regulatory pressures, such as Europe's reach authorization, and now by indirect pressures with the market itself [16].

The current industry considers phthalate concerns and attempts to use non-migrated phthalates on the surface of PVC products, but others are chemically tied. Replacing the migrated dioctyl phthalates with functionalized ones that bind to the PVC backbone kept plasticizing properties. The bio-based natural plasticizers, such as soybeans, require further investigation. The native low-cost construction PVC and its composites showed uneconomic recycling in comparison with the postindustrial substance of known composition. So, thermoplastics PVC is the least recycled substance, and substance brokers [17, 18].

Click chemistry is a one-step reaction with high yield, recently applied during the compounding of (bio-, natural, industrial) polymers into useful composites (advanced materials) with new, promising properties. This synthetic approach enabled scale-up functionalization, modification, and analysis. One-step compounding of plastics improved crosslinking (Scheme 1) and filler incorporation into the base polymer matrix [14]. For example, chitosan (CS) chemically cross-linked using glutaraldehyde, produces a drug carrier for the antiviral acyclovir drug which increases oral bioavailability. This one-step reaction without a coupling agent gives a CS-dimer Schiff base amorphous material containing a C=N imine group. The surface roughness and grooves increased the swelling ability compared to smooth-surface native chitosan. The swelling percentage increased with increasing the degree of crosslinking and improved drug release.

The low recycling rates of plastics range from 10% to 33%, although the widespread disposal of plastic wastes exacerbated the global pollution crisis [19]. While plastics offer unparalleled convenience, the adverse environmental aging consequences are increasingly evident [20]. Plastic waste is fragmented through mechanical dispersion, biodegradation, and photodegradation, forming smaller

(macro, micro, and nm) plastic particles [21]. MPs have particle sizes smaller than 5 mm or 1.0  $\mu\text{m}$  (the recent lower size limit reported according to the International System of Units (SI) nomenclature) [22].



**Scheme 1:** Chemically cross-linked chitosan with glutaraldehyde [14].

## 1.2. History of Plastics and Characteristics of Nanoplastics

Plastic-based products have become indispensable in our daily lives, with applications ranging from construction materials, pipes, and household goods to medical tools, agricultural components, personal care items, and even cosmetics. Since the 1950s, the mass production of plastics has steadily increased (especially for applications in healthcare and food products [23]), surpassing 400 million tons annually (Plastics Europe, 2024) [24]. Over the past five decades, global plastic production reached an 8.7% annual rate, resulting in an estimated cumulative 9.1 billion tons [25].

Nanoplastics are plastic particles ranging from 1 nm to 1000 nm in size, which are either directly manufactured or formed through the degradation of larger plastic debris. These particles exist as homogeneous or heterogeneous aggregates that exhibit unique colloidal properties, such as nm size and random Brownian motion [26]. Plastic degradation, driven by environmental processes such as photo- and thermal oxidation, is inherently slow over hundreds of years, making NPs a persistent environmental issue [27, 28].

Non-biodegradable plastics that accumulate in the environment progressively fragment into MPs and NPs, exacerbating ecological and health challenges [29]. NPs represent a hidden danger to people and the ecosystem [30], and in particular have garnered significant attention as an emerging environmental contaminant due to ease of absorption by organisms and higher ecological and toxicological risks compared to MPs [31]. The International Union of Pure and Applied Chemistry defined plastics as polymers enhanced with various additives to improve performance and reduce costs. The conversion of aged MPs into NPs is influenced by factors such as buoyancy and sedimentation [32].

Micro- and nano-plastics continuously move and are altered within the soil environment [33]. MPs and NPs form colloidal suspensions that significantly affect the chemical partitioning and sorption of organic and inorganic contaminants, altering their environmental fate and toxicity [34]. Due to their minute size, NPs are rapidly absorbed by organisms, translocating beyond the digestive tract and bio-accumulating along the food chain [35]. NPs are particularly toxic because they can penetrate biological membranes more effectively than MPs [36]. Researchers are increasingly studying the ecological effects of NPs, including impact on organism perturbations,

carbon sequestration, community dynamics, and overall ecosystem health [37].

MPs and NPs are pervasive contaminants found in indoor and outdoor air, water, sediments, soil, bottled water, and processed foods [38]. Alarmingly, MP is detected in organisms across various biological levels [39]. These pollutants are widely distributed through atmospheric deposition, ocean currents, water runoff, and winds, contributing to ecosystem degradation [40]. Poor plastic waste management intensified the release of MPs and NPs into wastewater systems from consumer products and further pollutes the environment [41-43].

Nanoplastics, characterized by their large surface area, can adsorb hazardous chemicals, acting as vectors for toxic metals and hydrophobic organic compounds. This exacerbates their harmful effects on biota and environmental health [42]. NPs are often derived from porous thermoplastic beads, such as PS cross-linked with divinylbenzene (DVB). Macro-porous resins formed through the polymerization of monomers dissolved in toluene or xylene are used in applications such as ion exchange and solid-phase synthesis. The limited or null swelling nature is suitable for continuous-flow synthesis, such as using a vehicle resin for organic paint coating [2, 43].

NPs are produced either mechanically *via* cryo-dry freeze or ball milling of various large plastic materials into fine powders to make the plastic brittle. In laser ablation, intense laser pulses break down plastic materials into NPs. Thin film deposition methods are either physical (physical vapor deposition (evaporation), sputtering (magnetron, radiofrequency, high energy ionic scattering)) or chemical deposition in either gas phase (chemical vapor deposition, electrochemical vapor deposition, and atomic laser deposition) or solution (sol-gel, deep coating, spin coating, and spray pyrolysis). The high internal surface area and chemical stability of NPs enabled diverse industrial applications [43, 44].

Cross-linked micro porous PS beads are synthesized *via* radical polymerization of micro emulsions of styrene and DVB. The bead size is controlled by the addition of surfactants (surface-active agents that give micelles) and optimal agitation. These beads demonstrated excellent swelling behavior in dipolar aprotic solvents due to non-covalent interactions within the PS matrix. However, water absorption swelling was less pronounced in protic solvents due to inherent hydrophobicity and chemical stability [45]. While cross-linked PS tolerates a broad range of reaction conditions, it can be chemically modified by strong oxidants at elevated temperatures that may degrade its aromatic benzene rings [46].

### 1.3. Nanoplastics as Carriers for Pathogenic Microorganisms and Excreted Antibiotics

Nanoplastics, like other surfaces, are carriers for pathogenic microorganisms, including bacteria and viruses, due to their high surface area and adsorption capacity [47, 48]. These particles facilitate the transfer of microorganisms from the surrounding environment to the human body, raising significant public health concerns. Infections caused by these pathogens remain a global challenge, necessitating novel antimicrobial strategies. NPs may also serve as adsorbents for multi-antibiotic-resistant bacteria further complicating this issue. Recognizing the hazards and toxicity of MPs and NPs,

the United Nations Environment Program (UNEP) classified them as emerging global environmental issues [49]. MPs and NPs are abundant in agricultural soils and aquatic ecosystems, yet international consensus on control standards is lacking. While some nations, including the UK, USA, New Zealand, EU members, and the UN, have banned the use of plastic microbeads in personal care products, efforts to mitigate NPs pollution remain insufficient [50, 51].

Among the most serious pathogens transported by NPs are viruses, which significantly contribute to global mortality [52]. A notable example is severe acute respiratory syndrome coronavirus-2 (SARS-CoV-2), the causative agent of COVID-19, which emerged in Wuhan, China, in 2019. This virus rapidly evolved into a pandemic, challenging healthcare systems worldwide. SARS-CoV-2 infects host cells by binding to the receptors of angiotensin-converting enzyme 2 (ACE2) expressed on pneumocytes, macrophages, and endothelial cells. The infection causes: respiratory impairment ranging from pneumonia to acute respiratory distress syndrome (ARDS), hypoxia, and type 2 myocardial infarction due to mismatched oxygen supply demand [53-57]. The hyperinflammatory state is characterized by the release of pro-inflammatory cytokines, including interleukins (IL-1, IL-6, and IL-7), tumor necrosis factor  $\alpha$ , and interferon- $\gamma$ . Cytokine storm damages endothelial function, promotes oxidative stress, and increases pro-thrombotic factors, contributing to vascular instability [58].

SARS-CoV-2 directly affects endothelial cells by interacting with expressed surface molecules. Inflammation by NPs enhances the instability of preexisting atheromatous plaques, promotes platelet activation and aggregation, and up-regulates the sympathetic nervous system, leading to elevated vasomotility and coronary spasm [59]. The interplay of all mechanisms may favor plaque rupture and thrombosis, leading to type 1 myocardial infarction: acute coronary syndrome and angiotensin ACE2. Failure to compensate for decreased oxygen transport under a concentration gradient is signaled by lactic acidosis, bradycardia, and decreased cardiac output. The latter effect develops rapidly, and all are indicators of impending tissue injury or death by hypoxemia. NPs increased the lifetime, spreading, and transport of viruses and pathogens [60].

NPs also play a role in gut dysbiosis during SARS-CoV-2 infection. The virus binds ACE2 receptors on enterocytes, disrupting the intestinal barrier and enabling the hematological dissemination of gut microbes [61]. This systemic inflammation leads to elevated levels of circulating pro-inflammatory cytokines, which can cross the blood-brain barrier (BBB), contributing to neuroinflammation and oxidative stress [61, 62]. Systemic inflammation increases the level of circulating reactive oxygen species (ROS) such as oxides, hydroxyl ( $\text{OH}^{\bullet}$ ), and nitric oxide free radicals, further affecting the brainstem and the cerebrum. The brain's limited antioxidant capacity causes oxidative stress, leading to neuroinflammation and mitochondrial DNA damage. An antiviral drug binds to and de-strands coiled DNA. Oxidative DNA cleavage by  $\text{OH}^{\bullet}$  occurs *via* hydrogen atom (H) abstraction from its sugar units and releases specific transformed sugar residues depending on H-position. Removal cleavage is inhibited by free radical scavengers, implying that  $\text{OH}^{\bullet}$  or peroxy derivatives (generated from the co-reactant hydrogen peroxide ( $\text{H}_2\text{O}_2$ )) mediate the cleavage

reaction. Patients given antioxidant therapeutic drugs are protected against both hazards:  $H_2O_2$  and ROS fragmentation [62].

The global impact of viral infections is magnified by the resistance to the existing antiviral drugs and the emergence of novel viruses, a phenomenon potentially accelerated by NPs pollution [63]. Viruses are obligate intracellular parasites that rely on host cells for replication. The development of broad-spectrum antiviral drugs is hindered by the specificity of viral replication mechanisms and the limited number of target viral proteins [64]. A limited number of viruses are targeted by antiviral drugs without harming the host [65]. NPs pollution influences the pharmacokinetics of antiviral drugs, with hydrophilic NPs being cleared from the human body more rapidly than hydrophobic variants [66].

NPs have also been shown to induce various forms of toxicity, including nephrotoxicity, hepatotoxicity, hematotoxicity, and testicular toxicity, as well as renal tubular necrosis. These effects are primarily mediated through interactions with nucleophilic components of cells, leading to apoptosis, oxidative stress, and oxygen-related genotoxicity in endothelial cells. Such mechanisms contribute to acute tissue damage and disruptions in normal physiological functions, often accompanied by increased lipid peroxidation. NPs have been reported to impair the function of vital organs such as the blood, liver, kidneys, and testes [49]. In particular, toxic NPs tend to accumulate in the liver until detoxification occurs. Hepatic toxicity can be monitored through liver transaminases, specifically aspartate transaminase (AST) and alanine transaminase (ALT), which serve as key diagnostic biomarkers. These enzymes are normally present at high concentrations in the cytoplasm, but during hepatocellular injury, they leak into the bloodstream in proportion to the severity of liver damage [61].

NPs enhance carcinogenicity by activating the PI3K/AKT3 signaling pathway. AKT3 exhibited more sensitivity to DNA methylation, compared to other genes (PIK3CA, IKBKB, and IL1B). The mRNA expressions of PIK3CA, AKT3, and IKBKB correlated with copy number variation (CNV) in human liver hepatocellular carcinoma (LIHC). The PIK3CA had the highest mutation rate among other genes of interest for LIHC. The intricate combined inherited and environmental factors (such as NPs pollution) cause tumors depending on age, gender, race (black, white), genetic mutation, family & personal history of cancer or certain non-cancerous breast disease, obesity, physical activity, hormonal intake, smoking, alcohol, and radiation exposure [61-65].

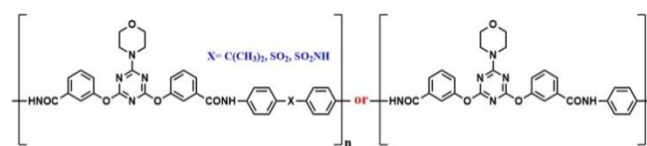
#### 1.4. Plastic Pollutants

Microplastics (MPs) and NPs in polluted water pose significant toxicity risks to marine organisms. Despite evidence of bioaccumulation and toxicity, few remediation and mitigation strategies have been reported [32]. The health risks and associated factors, though critical, remain underexplored in the literature [61]. NPs released into the environment from primary sources (materials manufactured for specific purposes, such as electronics, adhesives, anticorrosive protective coating, and medical equipment and radiation shields) and secondary sources [67] (ball milling the larger plastic items, from micro emulsion of polymer pieces' fragments, or originate naturally from the plastics' disintegration or degradation) [68]. The main sources of NPs pollution are the illegal discharge of non-biodegradable

plastics and the leaching of the binder (resins) from the anticorrosive coating from inshore and offshore marine infrastructure [67].

Plastic degradation involves chemical changes in the molecular structure, altering the material's properties. The degradation extent and mechanism depend on the chemical composition and structure of the plastic [69].

A potential solution to the environmental impact of NPs pollutants lies in the development of biodegradable polymers. By tuning the molecular structure, it is possible to improve the thermal and mechanical stability of these polymers as viable replacements for conventional plastics. Biodegradable polymers often contain heteroatoms, such as nitrogen (N), oxygen (O), and sulfur (S) distributed throughout the polymer chains. For example, polyamides (Figure 3) demonstrate excellent thermal stability and are applied in the automotive industry and marine engineering.



**Figure 3.** An example of a biodegradable polymer containing nitrogen and oxygen heteroatoms.

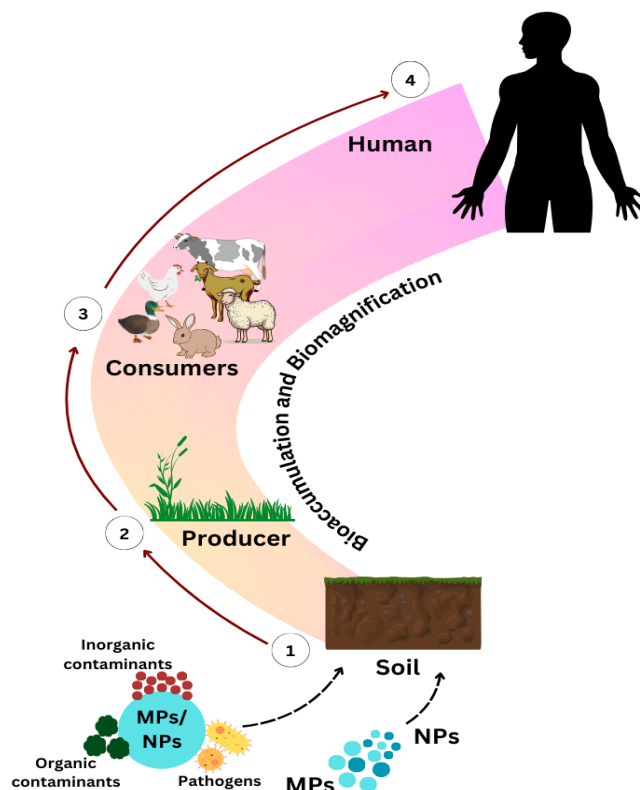
#### 1.5. Abundance and fate of nanoplastics

The continuous development of biodegradable polymers and maximizing their applications is required in all fields of technology [70]. High-molecular-weight (Mw) plastics pose relatively less concern in environmental settings [71]. However, NPs remain a significant environmental issue due to their potential harm to living organisms. The impact of NPs depends on various factors, including their sources (wastewater treatment plant effluents and wind-driven water currents), as well as particle size, shape, density, and chemical composition [72].

Compared to aquatic ecosystems, soil ecosystems present a more complex medium for the transport, bioavailability, and ecological impact of NPs. In soil ecosystems, NPs affect both individual organisms and the microbiome, altering ecological linkages and population dynamics (Figure 4). For instance, NPs have catastrophic effects on plants, particularly by interfering with the absorbed nutrients [73-75]. NPs may impact plants in several ways, including: declined shoot and root lengths, weight loss, reduced cell size, and smoothed chloroplasts. The grana lamellae may also become ambiguous and photosynthetic pigment content, such as chlorophyll (a, b) and carotenoid, may be altered (decreased total chlorophyll content corresponding to the increase in anthocyanin content). NPs can also decrease the carbohydrate and protein content in the plant, alter metabolism, and increase the phenol content. Increasing the levels of malondialdehyde and hydrogen peroxide decreases PS-II electron transport, and in turn increases proline content. The smaller particle size and the larger surface areas elevate the cellular uptake and toxicity of NPs [75].

Regulatory assessments of MPs and NPs in the United States and Europe highlighted the role of wastewater treatment plants (WWTPs) as significant sources of NPs contamination. During wastewater treatment, MPs are broken down into NPs,

which can infiltrate biofilms and contribute to environmental pollution [76, 77]. Additionally, the use of sludge from WWTPs, often contaminated with plastic wastes as fertilizer for crops in many countries, further exacerbates the dissemination of NPs in agricultural ecosystems [78].



**Figure 4.** Transfer of MPs and NPs in the soil ecos.

### 1.6. Nanoplastics transfer via fish migration

NPs are transferred within ecosystems through various mechanisms, including fish migration [78]. Many fish species migrate regularly between different parts of a water body for feeding, reproduction, or reasons that are not yet fully understood. The duration of these migrations can range from daily movements to annual or longer cycles, covering distances from a few meters to thousands of kilometers [79]. Fish migrations are classified based on movement between marine and freshwater. Anadromous movement from salt water into fresh water for spawning, while catadromous migrations occur in the reverse direction for similar purposes. Marine forage fish are extensively used for spawning, feeding, and nursery activities. These movements are often influenced by ocean currents and regions' seasonal food availability [80, 81].

The reasons for some migrations remained unclear; for instance, certain fish fail to recognize their offspring, prompting continued movement [82]. The United Nations Convention on the Law of the Sea identifies certain fish species as highly migratory, including anadromous species such as salmon, striped bass, lamprey, and catadromous species such as eels and diadromous bull sharks. These species often traverse the exclusive economic zones of multiple nations, and their management is addressed

differently under international treaties [83]. NPs are absorbed by marine organisms during vertical migrations. For example, fish feeding near the water/air interface at night ingest NPs before sinking to deeper water layers during the day [84]. Tuna and other species exhibit horizontal migrations (moving north and south in response to temperature gradients), which can influence the dispersal and transfer of NPs pollutants [85-87].

NPs released into the marine environment pose a negative threat to the marine ecosystem and can reach humans through the food chain. The toxicity to microalgae was explored as the generation of reactive oxygen species. The algae adsorb over toxic NPs, forming an eco-corona (decreased cell viability, membrane integrity, and photosynthetic yield). The oxidative stress: generated reactive oxygen species, hydroxyl, and superoxide specific radicals; inhibited antioxidant enzymes superoxide dismutase and catalase, depending on the surface charge of NPs and contact time [73].

### 1.7. Global legislative and institutional measures in plastic waste management

Among the global efforts to reduce the risks of marine NPs pollution, various regulatory frameworks have been implemented to manage plastic particle waste, including international agreements such as the "Stockholm Convention on Persistent Organic Pollutants (POPs)" [88]. Global legislative actions specifically targeted the restriction of microbead-containing products ( $\mu$ Bs). For instance, the  $\mu$ Bs-Free Waters Act in the United States and similar regulations within the European Union (a major  $\mu$ Bs producer) aimed to decrease their environmental impact. At the end of 2023, the European Commission adopted new regulations addressing plastic waste management [89].

### 1.8. Additives in nanoplastics

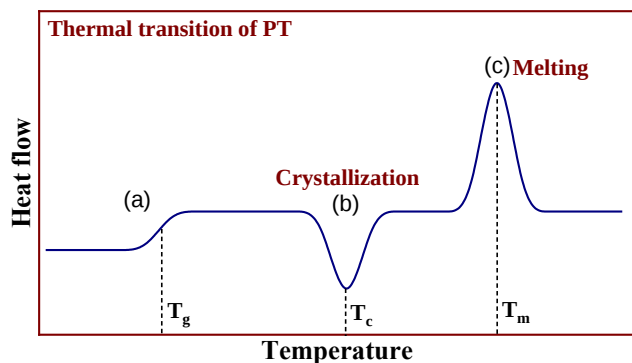
NPs derived from both primary and secondary sources pose greater ecological risks than MPs, impacting ecosystems, wildlife, aquatic and terrestrial environments, soil organisms, and agro-ecosystems [89]. NPs are commonly discharged into aquatic systems through materials like compounded plastic pipes, including PS and PVC [2, 15-18].

NPs are produced from polyethylene (PE) and polyethylene terephthalate (PET) by biological degradation, mechanical abrasion and friction, and chemical breakdown and degradation. These two thermoplastic resins (along with polycarbonate, polyvinyl chloride, acrylonitrile butadiene, polyethylene, styrene (ABS), polystyrene, nylon, and polyphenylene sulfide) are not common in compounding, where compressed, reformed, and reheated polymers attain another shape. Thermoset resins, phenolics, rubbers, vinyl esters, and polyesters are more easily compounded than thermoplastics (examples used in compression molded).

Polymers' additives enhance mechanical, electrical, thermal, and morphological properties. However, residual stresses at the polymer matrix/additive interface during curing can create micro-cracks and voids, reducing tensile strength. Composite polymers, though resistant to abrasion and biodegradation, further contribute to NPs' environmental persistence [90]. Additives in NPs improve various properties, including morphology, tensile strength, elongation at break, Young's modulus, electrical surface resistivity, volume resistivity, and thermal stability in terms of high glass transition ( $T_g$ ) and

decomposition ( $T_d$ ) temperatures [91]. The thermal response of plastics, as obtained from differential scanning calorimetry, is shown in **Figure 5**.

DSC explores thermal transitions, such as  $T_g$ , crystallization and melting. Above  $T_g$ ,  $C_p$  of the sample increased.  $C_p$  is measured at the middle of incline.  $T_{\text{crystallization}}$ : above  $T_g$ , mobility improved as kinetic energy increased motion in ordered crystalline arrangements which leads to released heat. The area under the crystallization peak gave exothermic  $\Delta H_{\text{crystallization}}$  transition. Endothermic melting above  $T_c$ . Temperature ( $T_m$ ) remains constant until complete melting. The area under the peak equals  $\Delta H_{\text{melting}}$  [91].



**Figure 5.** Sample response to temperature.

Glass transition involves no endothermic or exothermic peak as no latent heat is involved in or out of the system, only  $C$  change. On the other hand, melting and crystallization release or absorb heat, and therefore have latent heats.

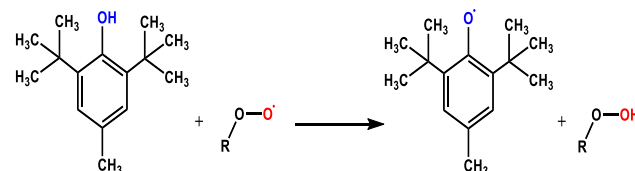
In NP microstructures, the polymorphic additives are uniformly distributed and strongly adhere with minimal voids, enhancing the abrasion resistance [92]. Additives influence properties, such as biodegradation, adhesion, wetting, friction, water absorption, chemical reactivity, and compatibility. These properties impact processing methods such as injection molding, thermoforming, extrusion, and aging. Additives are mechanically dispersed in the polymer matrix during melt-mixing via non-chemical bonds, but significantly affect performance [93]. NPs produced through mechanical dispersion and degradation during plastic manufacturing and service life [94]. The plastic's stability depends on chemical structure, manufacturing methods, and residual catalyst concentrations post-polymerization. For example, cobalt and chromium catalysts are used as both heterogeneous and homogeneous catalysts in plastic production, influencing plastic properties and environmental persistence [95].

### 1.9. High-speed mixers for polymer compounding

High-speed mixers in polymer compounding incorporate additives into a base polymer to achieve desired properties without altering its molecular structure [96]. Additives, blended with the base polymer and formulation components, create composites with enhanced characteristics. For example, compounding PVC resin with various additives produces a new composite that allows further processing. These efficient mixers contain fixed and movable parts, utilize low 0.75 kW energy power, and are equipped with an automatic dosing system of high-volume capacities, handling up to thousands

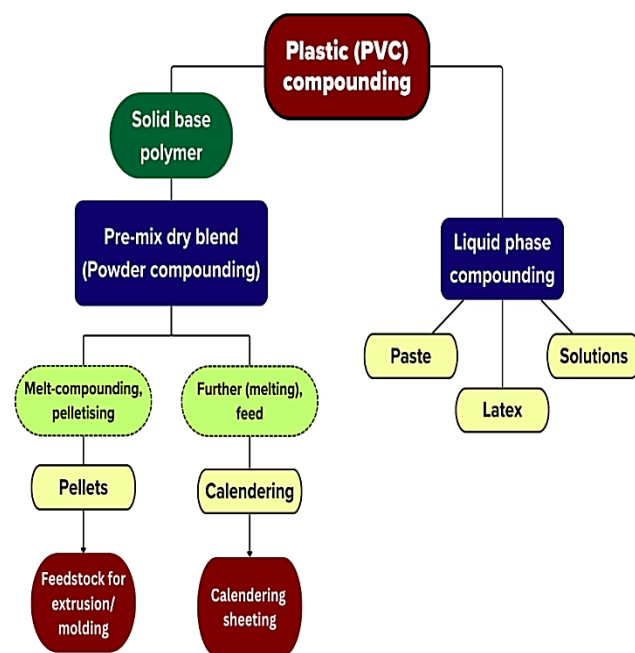
cm<sup>3</sup>/h, with dimensions: 1625 mm width x 1750 mm height [97].

Industrial batch mixing produces polymer composites in discrete quantities. Equipment like internal mixers and two-roll mills create thin composite films, further compressed into final composite forms [98]. Additives such as para-cresol (**Figure 6**), retarded polymer degradation. However, due to toxicity, this compound is banned in protective coatings [99].



**Figure 6.** Chemical structure of toxic para-cresol.

Dry blend thin film polymer samples were processed using oil-heated Brabender two-roll mills (model PM-3000) under controlled conditions. The samples were mixed at 200°C for 10 min. with a 30 revolutions per minute agitation speed. After processing, the compounded polymer was allowed to cool to room temperature and reweighed [100]. The mixing components are continuously fed into the machine, such as a single- or twin-screw extruder. The compounding steps include mixing (blending constituents into solid fine powder forms) and melting (into liquid composition (e.g., solution, latex, or paste), depending on the desired outcome [101], as illustrated in **Figure 7**.



**Figure 7.** Flow chart for additives-modified PVC (dry pre-blending with additives, then shear and heat are used to produce uniform pellets for further melting).

### 1.10. Role of additives in plastic processing and properties

Additives play a crucial role in improving the processing and performance of thermoplastics. They influence hot melt flow and rheology during injection molding, thermoforming, and

extrusion. Additives are mechanically mixed into plastics after polymerization. Thermoplastic composites often incorporate various additives to achieve desired properties either during processing or in subsequent formulations [102]. Additives interact physically and chemically with the plastic matrix and persist after plastic deterioration. Additives enhance characteristics such as thermal stability, impact resistance, flame retardation, photostability, aesthetics, and weathering resistance [103]. High-strength reinforcing inert fibers, such as carbon and glass, are often introduced into the polymer matrix to reduce the thermal expansion coefficient, while increasing modulus strength. These fibers do not typically increase density but can decrease impact resistance [104].

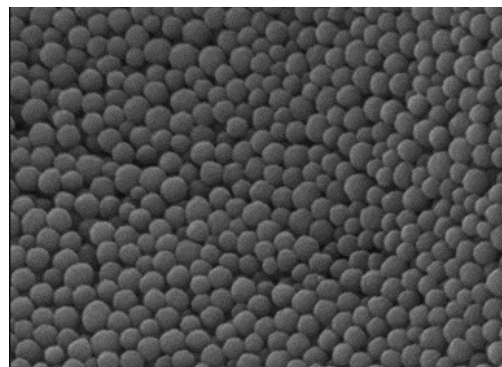
Granulated or flaked fillers reduce costs while increasing stiffness. Conversely, plasticizer additives improve flexibility, reduce modulus, and enable the customization for specific applications [103]. Polymorphous additives, mechanically dispersed within PS with non-chemical bonds, inhibited aging [104].

Technological advancements have enabled the rapid and precise determination of additives required to optimize both the processing and service life of plastic products. Additives in plastic composites contribute to economic efficiency, reducing costs of pipeline manufacturing, contours, and molding [104].

Instrumental techniques such as infrared Raman spectroscopy (detects functionality) and ultraviolet (UV) spectroscopy are employed in the characterization and quality control of plastics. The micrographs of scanning electron microscopy (SEM) revealed uniform additive distribution, strong constituent bonding, and good adhesion in such composite polymer blends. However, these methods are inaccurate in analyzing additives such as antioxidants or photostabilizers, particularly due to spectral frequencies overlapping [105]. The complex polymer/additive interface required advanced analytical techniques such as HPLC (sensitive detection with robust separation) to obtain specific and reliable analytical data. Such advancements are critical to overcoming challenges associated with the precise analysis of additives and plastics [106].

NPs are more disintegrated than degraded. Microplastic (MP) pollution produces particles smaller than 5 mm. The primary source of MP contamination in the seas is the degradation of plastic waste [107]. MPs are directly released into the environment during the production of micro-sized particles for various applications. The degradation and disintegration of MPs result in tiny particle sizes of 0.1  $\mu\text{m}$ , forming NPs. NPs typically have nanoscale dimensions and are often regularly spherical in shape, as shown in [Figure 8](#).

Thermoplastics are characterized by being amorphous or disordered in structure, soft and can easily melt to form new shapes on heating, but solidify upon cooling. Reheating and reforming make thermoplastics useful in applications such as hydrogen production. Spherical NPs are more hazardous than other shapes due to their smaller size (MPs (1  $\mu\text{m}$  - 5 mm) and NPs (below 1  $\mu\text{m}$ )) [108]. MPs gel-modified surfaces and interfaces serve various purposes such as hydrophobicity, anti-foaming, and mold-releaser. The transparent elastomers are used as stress-relieving interlayers in safety glass or plastic windshields [109].



**Figure 8.** SEM micrograph for NPs particles (Adapted with CCBY 4.0 permission [107]). Semi-crystalline morphology. Molding fabricated plastics into pellets.

### 1.11. Microplastics and nanoplastics in environmental and human health contexts

NPs pollution is largely produced from thermoplastics (short life time and more hazardous) than thermoset polymers due to wider applications), such as plastic packaging and most of the daily life purposes. NPs are extensively produced above  $T_d$  of the recycled thermoplastic (more common industrial uses and short life time than thermoset plastics) [91].

NPs caused significant anthropogenic changes to the Earth's surface. It has become one of the most pressing global concerns for biodiversity conservation. The accumulation of durable, aged, and persistent plastics in marine environments poses a significant hazard to biota. Despite its growing importance, the potential impacts of MP and NP pollution on biodiversity in continental systems remain largely under-investigation. Due to nm size, a substantial quantity of NPs is ingested by various marine organisms such as fish which are then consumed by humans through the food chain. NPs' concentration within fish tissues is amplified on moving up the food chain [110-112].

NPs are detected in aquatic environments and are now recognized as omnipresent contaminants that pose potential risks to both aquatic organisms and human health *via* the consumption and ingestion of contaminated fishery products (primary exposure route of NPs besides contaminated water). Once ingested by oral uptake [113], NPs pass through the gastrointestinal tract (GIT) and are absorbed, leading to oxidative stress, cytotoxicity, and translocation to other tissues. After absorption in the GIT, NPs penetrate biological membranes *via* passive diffusion under concentration gradients, following Fick's law of diffusion. NPs traverse the lumen and gut wall, followed by penetration of the epithelial membrane into systemic circulation capillaries, as represented in [Figure 9](#).

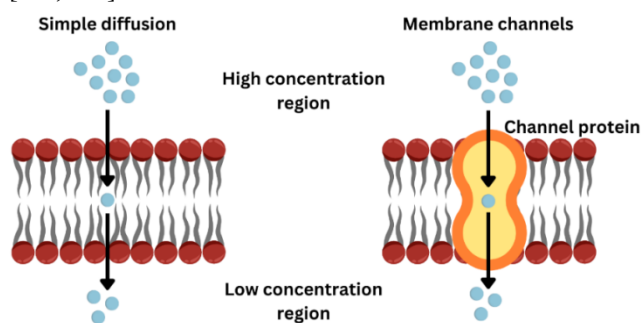
The mass transfer of NPs depends on the membrane's area and thickness, as well as the partition and diffusion coefficients. Upon entering the bloodstream, NPs are rapidly distributed throughout the circulatory system. Due to the significant volume differences between the absorption site and the distribution sites, NPs' concentration in blood ( $C_b$ ) is lower than the NPs' concentration at the absorption site ( $C_{abs}$ ) [114].

The passive diffusion absorption has a first-order kinetics. The absorption rate ( $dC/dt$ ) is directly proportional to  $C_{abs}$  and

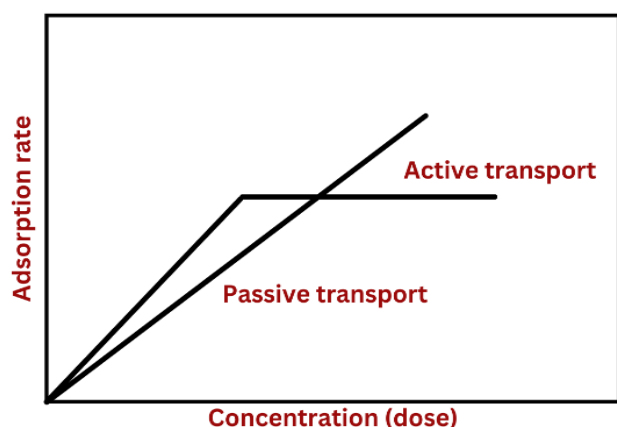
increases linearly with the NPs' concentration. High  $C_{abs}$  increased the absorption rate.

$$\text{Kinetic equation: } \frac{dc}{dt} = k(c_b - c_{abs}) \quad (1)$$

A major source of variation in NPs absorption is membrane permeability, which depends on the NPs' lipophilicity that enables their partition between oil and water. The lipid solubility of NPs is a critical physicochemical factor that facilitates their penetration through various biological membrane barriers. High partition coefficients enhance the absorption of electrically neutral NPs, particularly from the colon biological fluid. Although most NPs are passively absorbed, a carrier-mediated or active transport mechanism is probable if the NPs are structurally similar to the substrates typically transported across membranes. Active transport also occurs against a concentration gradient, but it is limited at high concentrations due to insufficient carriers [115]. Competitive absorption due to similar molecular structures decreases the NPs' absorption rate. Hydrophilic NPs with chemical structures resembling endogenous substances utilize GIT transport systems. At sufficiently high concentrations, these transport systems become saturated. Unlike linear passive diffusion, active transport exhibits a curvilinear dependence on concentration as illustrated in Figure 10 [114, 115].



**Figure 9.** Schematic representation of intracellular passive NPs bio transition.



**Figure 10.** First-order kinetic plot of NPs' passive tr.

Electrically neutral ion-pairs (water-soluble, lipophobic NPs) cannot be directly absorbed from the GIT. Strong electrolyte NPs, such as quaternary ammonium (NPs) halide molecules, maintain their charge across all physiological pH levels, limiting their ability to penetrate biological membranes.

However, binding of ionized NPs to counterion complexes facilitated their diffusion across membranes [116].

Convection absorption involves the transport of small molecules (molecular radii  $< 4.0 \text{ \AA}$ ) through water-filled pores in biological membranes. The rate is determined by the product of the sieving coefficient (characteristic for the relative sizes of pores and molecules), the physiological fluid absorption rate, and the solute concentration in luminal content [117]. Hydrophilic, multifunctional, and large-sized polar NPs that lack structural similarity to endogenous substances cannot actively transport in the GIT. Their large size and lack of compatibility with transport systems prevent oral absorption, which is affected by several physicochemical factors, including the pH-partition theory of biological membranes as lipid barriers. The lipid solubility of NPs determines their ability to penetrate membranes. Dissolution and pH influence ionization and stability, whereas complexation and adsorption affect NP bioavailability [114, 115].

The nonionized acidic or basic NPs are preferentially absorbed by passive diffusion, with absorption (rate and amount) depending on the oil-water partition coefficient (the more lipophilic the NPs, the faster is its absorption). Weak acidic and neutral NPs are absorbed in the stomach, while basic NPs are absorbed in the intestines [118]. MPs and NPs have a high likelihood of ingestion, incorporation, and bioaccumulation in tissues of various organisms. Plastic particles are concentrated in the digestive tract; however, smaller particles (MPs, NPs) persist in the animal's body and translocate from the intestinal tract to the circulatory system or surrounding tissues [119].

Plastic contamination in the food chain has steadily increased. In the 1960s, MPs were first observed in the guts of seabirds, and their presence in marine ecosystems has escalated. In 2023, the new plasticosis disease was caused solely by plastic ingestion in seabirds. Symptoms include chronic inflammation and scarring of the digestive tract. Persistent inflammation over time disfigures tissues and impairs digestion, growth, and survival [120].

#### 1.12. Bioaccumulation in seafood, safety, and human health

MPs are highly persistent pollutants that have infiltrated all compartments of marine ecosystems, including the food web. MPs accumulate across different trophic levels in marine organisms such as bivalves, crustaceans, and fish. These particles are found in various body parts, including the GIT, liver, and gills, raising concerns about seafood species that are consumed whole, such as bivalves, some crustaceans, and some small fish; or just in flesh parts, such as larger fish [120].

Human exposure to MPs varies by geographical and cultural dietary habits. In eviscerated fish, direct exposure to MPs is relatively low; however, this does not eliminate the risk. A study on dried fish species, sin croaker "*Johnius belangerii*" and greenback mullet "*Chelon subviridis*", revealed that gutted fish contained more MPs than excised organs (viscera and gills), indicating partial mitigation of the risk of human intake [120].

MPs  $> 11 \mu\text{m}$  were first detected in the edible tissue of the squid *Uroteuthis (Photololigo) duvaucelii*, where MPs were found in 18% of the samples and an average of  $7.7 \pm 20$

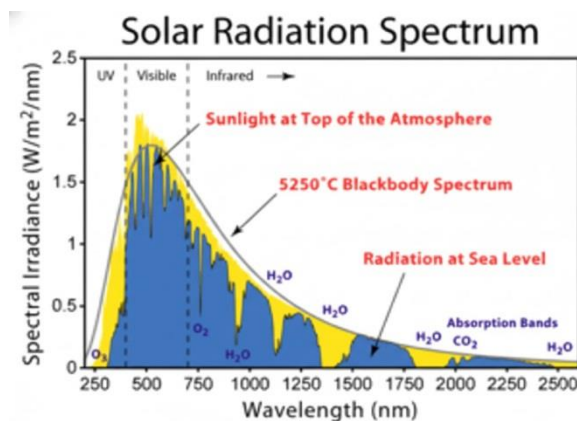
particles  $\text{kg}^{-1}$  edible tissue. MPs were found in 13.3% of blue crab *Portunus pelagicus* samples, averaging  $3.2 \pm 10$  particles  $\text{kg}^{-1}$  edible tissue. The annual MPs' dietary intake for shellfish consumers is estimated at  $13 \pm 0.58$  particles per capita/year [121,122].

According to the recommendations of the European Market Observatory for Fisheries and Aquaculture Products (EUMOFA), EFSA, and NOAA for fish consumption by humans at different ages, MPs intake calculated based on the ingestion of three fish species that are caught and commonly consumed, "*Dicentrarchus labrax*, *Trachurus*, and *Scomber colias*", varies from 112 to 842 particles/ year according to EFSA and from 518 to 3078 particles/year/ capita according to the EUMOFA and NOAA [123].

Bivalve molluscs are particularly prone to MP particle accumulation and transfer to humans through the food chain. Countries with high bivalve consumption, such as **China, South Korea, France, and Greece**, face high risks of exposure. An analysis of *D. trunculus* specimens collected along Italy's Tuscan coast revealed a total of 85 MP items (52.94% fibers and 47.06% fragments) in 39 samples. The dominant MP types were PE and PET, accounting for 83.33% of the particles. Consumers of *D. trunculus* tolerated ingestion 19.2 MPs/capita/year [124]. More in-vivo studies are required on the mitigation of cytotoxicity to humans by the uptake of medicinal plants [125].

### 1.13. Mitigation strategies for plastic photodegradation

The Earth receives  $1.8 \times 10^{17}$  W solar radiation at the top of its atmosphere, **Figure 11**. Half of this radiation reaches the Earth's surface because of light absorption, scattering, and reflection during the passage through the atmosphere. The shortest wavelength (the highest energetic UV-photon) causes photodegradation of plastics [3].



**Figure 11.** Solar radiation spectra observed both above the atmosphere and at the Earth's surface.

Trace graphene (G)-based materials at 1.0 Wt. % concentrations are photo stabilizers to plastics against photo degradation, particularly in marine coatings [126]. Graphene's abundant  $\pi$ -bonds and  $\text{sp}^2$  active sites of the carbon atom efficiently absorb UV. The high surface area and 2D geometry shield UV and oxygen. It is also a nucleating agent that improves the photostability of plastics and increases  $T_g$  and crystallinity. Graphene's photostabilizing ability is due to the activity of its  $\text{sp}^2$  sites rather than the surface OH groups in graphene oxide (GO) and reduced

graphene oxide (rGO). Polyaniline-modified GO synergistically enhances photodegradation resistance while improving weathering and corrosion resistance.

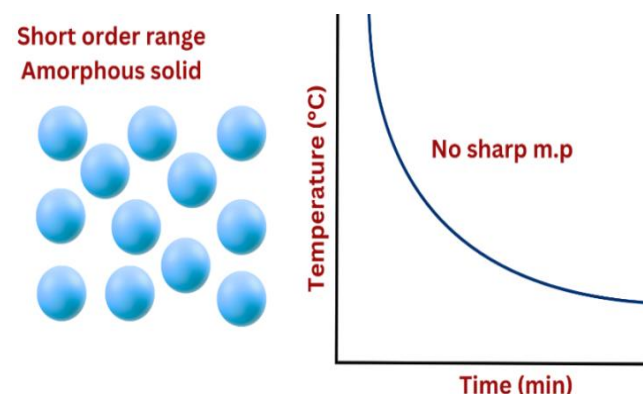
The incorporation of Fe carbonyl flakes into epoxy coatings blocks UV radiation. Curcumin siloxane composites deposited on polyester improved photodegradation resistance [2]. rGO nano platelets have been incorporated into PU nanocomposites to maximize resistance to sunlight and free radicals [126].

In multifunctional epoxy coatings, ceria-modified GO nanosheets shielded UV radiation. Similarly, hybrid graphene and carbon nanotube (CNT) fillers, in a 1:10 ratio, protected waterborne polymer composites from UV degradation. 1.0 Wt.% filler provided uniform dispersion and strong photoprotection. Beyond UV resistance, titanium and polydopamine-modified boron nitride (BN) enhanced flame retardancy via  $\pi$ - $\pi$  non-covalent interactions between polymer chains and hexagonal BN crystals. These modifications also generate  $\text{TiO}_2$  and pyrophosphate at high temperatures, which enhance mechanical strength. Additives effectively enhanced the strength and oxidation resistance of the char layer and improved thermal and air oxygen resistance [126].

Functionalized metal oxide nanoparticles such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , PbO, SnO, NbO, ZnO, and  $\text{TiO}_2$  are efficient photostabilizers for polymers.  $\text{TiO}_2$  is a cheap, abundant, and non-toxic semiconductor material that exists as (rutile, anatase, and brookite) crystals. The high 3.2 eV band gap of anatase made it chemically and photochemically more stable at low temperature [14].

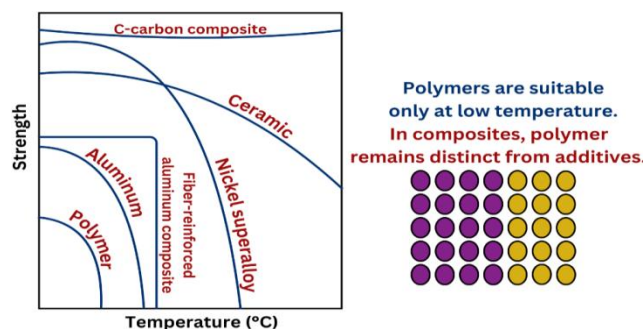
### 1.14. Some reasons for plastic degradation

Plastic composites are amorphous materials that lack long-range ordering (**Figure 12**). Since they are prepared by rapid cooling of the molten materials, there is no sufficient time to pack into a more thermodynamically favored crystalline state. Plastics are pseudo-solids that have an indefinite melting point (m.p.). By random arrangement, plastics are distorted, bent, and compressed. Amorphous solids are isotropic with equal-valued properties (thermal conductivity, refractive index, coefficient of thermal expansion, and electrical conductivity) in all directions.



**Figure 12.** Crystallinity and indefinite m.p. of polymer plastics.

As the temperature increases, strength of polymer decreases, **Figure 13**.



**Figure 13.** Variation of strength of some solids and composites with temperature.

The lowest thermal outstanding shown by the polymer is due to the irregular unsymmetric geometrical shape, no shared intermolecular forces, and low rigidity.

#### 1.14. Occupational Safety and Health Management

Industrial milling of both rubber and plastics, followed by ASTM-D1692-68 Test for flammability of low-melting material (containers, sheets, and cellular) plastics, creates hazardous conditions. Aerial equipment's Windows of the buildings are made from fiberglass-reinforced plastic and plastic in metal frames, respectively [127, 128]. Special consideration is given when plastics soften on fire exposure. Plastics designed in above-ground piping systems or inside buildings are protected against fire, or so located that any spill from failure of these materials could not unduly expose persons, buildings, or structures controlled by remote valves. NPs during polymer compounding or coating formulation are hazardous to some degree, and these hazards need protection from accidental skin, eye, and respiratory contact. Material Safety Data Sheet (MSDSs) collected information on physical properties, health hazards, reactivity, and spill cleanup procedures [129].

Flammability measures plastic ignition and fire spreading rate, and increases with increasing ignition tendency. The combustion of vapors of the hot melt plastics depends on the flash point and volatility (boiling point) at which hot melt plastics vaporize in quantities significant enough to form an ignitable mixture with air oxygen at a temperature above a flashpoint [130]. Flammable hot melt plastics such as polyester should never be stored near acids, stored in an area cooled enough to prevent ignition if mixed with air vapors. Adequate ventilation prevents vapor buildup. Avoid storage in conventional non-explosion-proof refrigerators. Sparks generated by internal lights or thermostats may ignite flammable plastics inside the refrigerator, causing an extremely dangerous explosion hazard. Storage areas should have spill-cleanup materials and proper firefighting equipment nearby. Portable fire extinguishing equipment should include dry chemical, foam, and carbon dioxide extinguishers. Storage is kept to a minimum [130].

"No Smoking signs are clearly posted at plastic use or storage. Flammable hot melt plastics are separated into categories and classes: I (A, B, C), II, III, based on flash points. The level of MP was classified as level III (moderate) [131].

MPs and NPs are handled using rubber gloves and safety goggles. Wear adequate protective equipment (Lab apron and

splash-proof eye protector). If splashing is a definite hazard, face shields must also be worn. The subsequent response by experimental animals helps predict the extent of NPs cytotoxicity in case of the administration of a particular NPs dose. The administration of a particular NPs dose and the subsequent response by experimental animals help predict of NPs cytotoxicity [130].

Dispensing of flammable hot melt plastics should only be carried out under a fume hood or in an approved storage room. When transferring or using flammable plastics, all area is evacuated from ignition sources. Proper grounding is used when transferring flammable plastics. Open flames or hot plates should not be used to directly heat flammable plastics, and water should not be used to clean up spills from flammable plastics. Flammable plastics (sources of combustible liquids) are not disposed of in the sinks or drains [132].

In the in-vivo experiment, dose-response behavior is represented by a dose-response plot. Since the individual's animal varies in response to a particular NPs dose in the same manner and differs in sensitivity and lethal dose, the average toxicity is denoted. The lethal chemical dose  $LD_{50}$  (mg NPs ingested/kg body weight) where 50% of test animals death by dosage. The lower  $LD_{50}$  reflected the higher toxicity. The NPs toxicity *via* absorption can be determined in several ways [113]. The threshold limit values will have a skin notation, indicating rapid absorption by the skin. Acute toxicity has immediate effects on the health of an over-exposed individual. Chronic toxicity due to long-term exposure. The 8-hour total weight average (TWA) permissible exposure is the average NPs concentration to which a worker can be exposed throughout an eight-hour workday without adverse effects. Short-term exposure limit (STEL) is the maximum amount to which a worker is exposed in fifteen minutes. period without adverse effects [49, 76, 113, 133, 134].

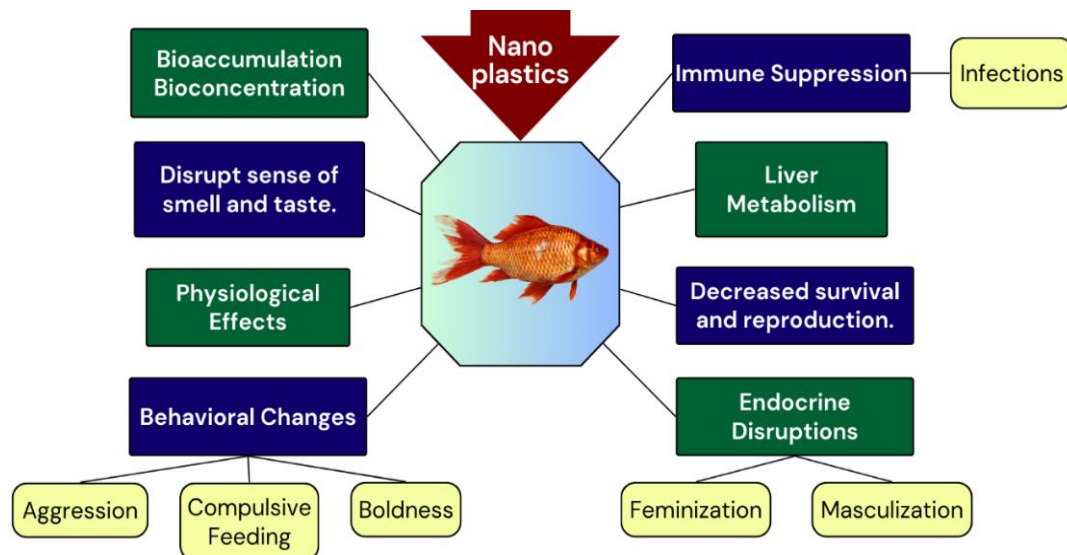
## 2. Discussion

Nanoplastics, derived from the degradation of MPs, are increasingly abundant in marine ecosystems, primarily originating from the breakdown of larger plastic items like bags, bottles, and fishing gear, as well as industrial activities and personal care products containing MPs. These particles are toxic to aquatic life, including fish, invertebrates, and algae, and can bioaccumulate in organisms, causing potential long-term health risks *via* interference with essential biological processes such as reproduction, growth, and development. Nevertheless, challenges in their monitoring and quantification persist due to their nanoscale size and complex nature [37, 59].

Fish populations and aquatic ecosystems suffer significant impacts from NPs as summarized in Table 1 and Figure 14. NPs disrupt liver fish metabolism, and humans consuming NPs-contaminated seafood are exposed to long-term health risks. Endocrine disruption, caused by PE, leads to masculinization and feminization in fish [111]. However, further research is needed to fully understand the long-term impacts of NPs. The toxicity of NPs depends on the size, chemical structure, chemical composition, and concentration of the NPs in marine environments, as well as the fish (species and life stage).

**Table 1:** Types of toxicity of nanoplastics in marine life [111]

| Fish physiology                                                                                                                                                                                                                             | Fish behavior                                                                                                                                                                       | Ecology                                                                                                                                                                                                                  |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Harming cells and tissues, impaired growth and fertility, and increased mortality. Bioaccumulation causes bio magnification in the food chain and threatens humans. Triggering inflammation, immunity disruption, diseases, and infections. | Altered feeding, swimming, and social interactions. Decreased survival and reproduction. Interfere with the sense of smell and taste. Hindered food finding and avoiding predators. | Cascading effects on aquatic ecosystems, disrupting food webs, and affecting overall health and marine biodiversity. Accumulation in sediments and aquatic habitats degrades the quality and decreases fish populations. |

**Figure 14.** Some impacts of nanoplastic pollution.

The nm size of NPs enhances their penetration of biological barriers, posing unique risks to human health and aquatic ecosystems. These risks are magnified for NPs by the interference of other pollutants such as heavy metals, discharged drugs, and organic matter, increasing their toxicity [61].

NPs are removed from wastewater using fine gratings, aerated grit tanks, coagulation sedimentation, biological degradation, sequencing batch reactor (SBR), membrane bioreactor, sand filtration (SF), and dissolved air flotation. The biological treatment stage depends on the adsorption of activated sludge, which is hindered by the presence of NPs. Hence, adsorption, membrane ultrafiltration, and advanced oxidation processes are good alternatives. The operational conditions are optimized to achieve complete efficiency. The most efficient technique is electrocoagulation [112].

Despite obstacles in assessing the risks posed by NPs due to insufficient data on their occurrence, distribution, and toxicity, previous studies identified potential hazards, including bioaccumulation and persistence in the marine environment. Quantifying exposure levels through ingestion, inhalation, and dermal absorption, and evaluating associated health risks, remains critical. Developing mitigation strategies such as implementing regulations, promoting sustainable consumption, and advancing innovative management technologies is essential for effectively addressing the NP pollution [40].

The maximum permissible limits (MPL) of NPs and MPs are

still unreported because their quantification in the discharged wastewater requires further studies and advanced technologies. The thousands of plastic factories (huge industry) produce waste a recycled after use (circular economy approaches: for the management of solid wastes in recovery into useful biodegradable products. In the US, for every ton produced, 20% is recycled and 80% is processed into the chemical plants. The consumed plastic not version (i.e., compounding with additives that decreased photo- and thermal degradation [134].

NPs affect workers in factories (explosion or death). The hazards of NPs follow the order: PS < PET < PVC < PP < PE (Chromium (Cr(III)) catalyst converted into Cr(IV) intermediate carcinogenic and causing death. The less toxic Al-Ti catalyst is under investigation. In PE polymerization, no catalyst is required. NPs produced from fuel cracking into hydrocarbons that polymerized and were compounded with dyes (improved color).

Future research needs to focus on understanding the NPs' cytotoxicity, monitoring exposure levels in industries, studying the fate and transport of NPs in freshwater and marine environments, and exploring innovative mitigation approaches. Comprehensive studies on NPs' interaction with gene expression in organisms, such as the overexpression of sugar biosynthesis genes and the formation of hetero-aggregates with specific polymers like polypropylene, will enhance our understanding of their environmental impact. As scientific knowledge advances, more effective risk

management strategies can be implemented to mitigate the adverse effects of NPs on ecosystems and human health [62].

NPs have a serious, harmful negative impact on human health. In vitro and in vivo studies confirmed oxidative stress, inflammation, carcinogenicity, cytotoxicity, and genotoxicity. Exhaled breath condensate (EBC) can provide precise information on the respiratory tract microenvironment. In field studies, 80 workers exposed to nanomaterials were examined. Exposure levels were assessed through epidemiological questionnaires, environmental measures, and HBM. The latter was implemented on non-invasively collected biological samples (urine, EBC), and by means of advanced analytical methods such as Real-time polymerase chain reaction (PCR), high-sensitivity Enzyme-Linked Immunosorbent Assays (ELISAs), and Nanoparticle Tracking Analysis (NTA) [1, 29], the number of particles in EBC was analyzed for the first time in a multicenter study to identify additional internal dose biomarkers not yet investigated in the literature. The significant relations between particle concentration, inflammatory cytokine levels, and oxidative stress in EBC suggest that exposure to MNPs modulates inflammation and oxidative stress levels. EBC and NTA effectively assessed internal dose and associated risks. A second field study was conducted on a cohort of 53 workers exposed to nanomaterials. Exposure levels were assessed through epidemiological questionnaires, and both urine and EBC samples were collected. Reported analytical techniques such as ELISA, qPCR-ELISA, and NTA, inflammatory biomarkers (cytokines), and oxidative stress markers were used. This work has not yet been published; analyses are still ongoing. However, preliminary results have revealed significant associations in levels of inflammatory cytokines and oxidative stress markers between exposed and non-exposed individuals, respectively, in EBC and urine samples. Findings provide a foundation for developing prevention and monitoring strategies for MNPs exposure, contributing to a better understanding of the impact on human health [1].

The modified sustainable biocompatible geopolymers (GP) can be used as an alternative to plastic-based organic coatings for mitigating marine pollution by NPs. GP (aluminosilicate) eco-friendly binder requires organic modification to exfoliate its nm layers [135]. The safe coating is formulated from a blend of organo-modified GP with safe synthetic polymer binder resins such as Teflon (poly tetrafluoroethylene or PTFE) or a modified biopolymer such as chitosan.

### 3. Conclusion

Nanoplastic pollution significantly harms marine ecosystems, including water, sediments, and marine organisms, and contributes to the shortage in fish production. This review highlighted the importance of raising awareness within the scientific and societal communities about the necessity of addressing NPs pollution, particularly through cleaning eaten marine fish and wastewater treatment to protect human health. While efforts have been made to establish a comprehensive policy framework to mitigate micro- and NPs plastic pollution, further research is essential for effective pollution control. The environmental cycle of NPs remains largely unknown, limiting our ability to conduct reliable risk assessments for human health. Current data are insufficient to evaluate the full extent of human exposure and the associated risks. Further studies on the kinetics and cytotoxicity of NPs are critical to understanding their long-term effects.

Additionally, the impact of NPs on the food chain and their potential accumulation in human diets are poorly understood. Comprehensive research on these aspects is necessary to assess the implications for human health accurately and to develop effective strategies to mitigate their adverse effects. Due to the health impact of the plastics industry, especially those utilizing chromium catalysts, which require the application and use of preventive measures and procedures (pillars and recyclers) to extinguish fires, extensive application of health, safety, environment, and quality (HSEQ) guidelines is required

#### List of abbreviations

NPs: Nanoplastics; MPs: Microplastics; PP: Polypropylene; LDPE: Low density polyethylene; HDPE: High-density polyethylene; PE: Poly ethylene; NPs: Nanoparticles; DINP: Diisononyl phthalate; DPHP: Dipropylheptyl phthalate; DEHP: Diethylhexyl phthalate; PVC: Polyvinyl chloride; PU: Polyurethane; PET: Polyethylene terephthalate; PS: Polystyrene; PA: Polyamide; Tg: glass transition temperature; DIDP: Diisodecyl phthalate; DBP: Dibutyl phthalate; BBP: Butyl benzyl phthalate.

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