

SUSTAINABLE APPROACHES IN POLYMERIC NANOCOMPOSITES REINFORCED BY METAL OXIDES

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ABSTRACT

Polymeric nanocomposites have aroused considerable academic and industrial interest due to their unique properties and applicability in several areas of chemistry, biotechnology and materials engineering. Their applications vary depending on the type of polymers, fillers, and incorporation method being used. However, many of its raw materials and ways of obtaining it are not sustainable. In this context, biodegradable nanocomposites, those obtained from renewable sources and those that incorporate metal oxides produced by the green route emerge as a promising alternative by bringing together improved properties, economic viability and high potential to contribute as a new technology to society, without harmfully compromising environmental resources and future generations. This review aims to analyze studies that portray these more sustainable forms of polymer-based materials and metal oxide nanoparticles. Thus, in addition to the materials chosen by various study groups, the most relevant preparation methods and characterization techniques in this context are discussed. The main properties and applications of these nanocomposites in various areas are also explored, including electronics, medicine, water treatment and purification methods, coatings, catalysts, sensors, solar cells, and energy storage devices. Finally, by addressing the future perspectives and challenges to be overcome for the widespread adoption of these materials, it is concluded that sustainable polymeric nanocomposites reinforced by metal oxides have great potential in several areas of the industry due to their improved mechanical, thermal and functional properties. However, its widespread adoption still faces significant challenges, especially related to the compatibility between the matrix and the booster, high production costs, complexity in processing and scaling, in addition to the urgent need to assess environmental and toxicological impacts to develop specific standards and legislation. Overcoming these barriers is possible, but it will require continuous advances in research and collaboration between academia, industry, and regulatory bodies, ratifying the relevance of this review.

Keywords: Nanocomposites. Polymers. Metal Oxides. Sustainability.

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INTRODUCTION

The nanoscale allows the application of peculiar physical and chemical properties, the result of both predicted events due to the expansion of the relative surface area, with the increase in the possibilities of interactions, and of the different physical processes that act on systems that approach the quantum scale. Such processes are, in fact, the same ones that enhance the complexity of biological life, with cells naturally demonstrating very high-efficiency processes that are only possible due to the scale at which they occur, and precisely for this reason, there is a laboratory race to mimic them (NASROLLAHZADEH et al., 2019).

An example of a very useful application of nanotechnology is the production of nanocomposites based on polymers, organic macromolecules composed of covalently linked repetitive subunits. This application involves the incorporation of nanometer-scale materials in polymeric matrices, to improve or confer new properties to polymers, through various methods such as the dispersion of nanoparticles via polymeric solution or fusion, the creation of interpenetrating polymeric networks, electrospinning and in situ polymerization (KRISHNAMOORTI; VAIA, 2007; KHAN et al., 2023). The benefits of nanotechnology applied to polymers are varied: mechanical properties such as tensile strength, hardness, and elasticity can be significantly improved. Thermal properties, including thermal stability and resistance to thermal degradation, as well. In addition, the electrical and optical properties of polymers can be adjusted, increasing electrical or thermal conductivity and modifying optical characteristics for applications in sensors and electronic devices. In addition, the barrier properties of polymers are strengthened, improving resistance to gas and liquid permeation, which is particularly useful for food, cosmetic, and pharmaceutical packaging (Handbook of Polymer and Ceramic Nanotechnology, 2021; Advanced Polymer Nanocomposites, 2022).

Examples of natural and synthetic polymer matrices, respectively, include: starch, silk, cellulose, keratin, proteins, and deoxyribonucleic acid (DNA); polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polystyrene (PS) and polyamide (PA). Although they are all polymers, each material is distinguished from the others both in its form of presentation and in its function. This is due to the fact that the properties of a polymer depend on several factors, such as molecular structure, methods used in obtaining or synthesizing, types of monomers in the composition and how they are chained, other substances present in the processing, storage and use conditions (MANO; DAYS; OLIVEIRA, 2004).

The importance of synthetic polymers to modern life is undeniable. Since the creation of conventional synthetic polymers and the subsequent start of mass production during the 20th century, billions of tons of materials have been produced for use in computers, vehicles, home décor, and many other areas, making them essential parts of how today's world works. Polymers are highly versatile and advantageous, as they can be molded into different shapes and sizes, resulting in materials that, even though they are lightweight, generally have high chemical resistance, durability, electrical and thermal insulation capacity, low production cost, ease of processing, as well as resistance to corrosion and impact. These properties make polymers a preferred choice for a wide range of applications such as packaging, electronics and components of the most diverse for the automotive and aerospace sectors (MANO; MENDES, 1999; MANO, 2000).

However, despite their great versatility, it is important to emphasize that polymers are not a universal solution. Just like any material, they have limitations in their applications. These include the low temperature resistance compared to metals, the possibility of degradation when exposed to harsh environmental conditions such as UV light and humidity, and the concern about environmental pollution due to its slow rate of degradation under improper disposal conditions. Additionally, in some specific applications, some polymers may not offer the required mechanical properties, resulting in performance limitations. These drawbacks highlight the importance of carefully considering the characteristics and conditions of use of polymers and their combinations in different applications, to mitigate potential issues and maximize benefits. In addition, it is possible to circumvent many of the limitations of certain polymeric matrices with the use of nanotechnology (MANO, 2000; NJUGUNA; PIELICHOWSKI; DESAI, 2008; RALLINI; KENNY, 2017).

Nanoparticles (NPs) are structures whose properties differ from the usual scale (whether microscopic or macroscopic) due to the size reduction, said at the nano scale between 1 and 100 x 10-9 meters, in at least one of their dimensions. Their diminutive size grants them peculiar properties, such as very high reactivity and prevalence of quantum properties. Also extremely prevalent in modern life, they are found in the form of NPs of metal oxides, already incorporated into several commercial products such as: sunscreens (Titanium oxide), drugs with drug delivery technology (Iron oxide), solar panels (Zinc oxide) and cancer treatments (Copper oxide) (EL-NAGGAR et al., 2016; GHOSH et al., 2019; MONTIEL-SCHNEIDER et al., 2022; TABREZ et al., 2022).

By inserting nanoparticles into the polymeric matrix during the process of creating a

product, it is possible to add, remove and modify certain properties of the material, generating polymeric nanocomposites (NCPs), extremely versatile materials of high interest to the scientific and technological community. This is reflected in the fact that this is a highly active branch of study, with continuous discoveries and innovations, with the NPs of metal oxides acting as mechanical reinforcement, in improving wear resistance, increasing thermal and flame resistance, adding optical, antimicrobial and barrier properties. However, the dissemination and deepening of so many studies brings with it concerns: with a growth in popular and academic focus on the topic of sustainability, criticisms have been made about the feasibility of the extensive use of polymers, NPs and NCPs, given their impact on the world (AVÉROUS; POLLET, 2012; GUILLET, 2012; YIN; DENG, 2015; NASKAR; KEUM; BOEMAN, 2016; KHALAF, 2016; WRÓBLEWSKA-KREPSZTUL et al., 2018; FU et al., 2019; WANG et al., 2020; DA ROCHA et al., 2024 a,b).

In fact, many of the ways of obtaining, producing and consuming the three materials mentioned (polymers, NPs and NCPs) are unsustainable. For example, the main group of modern polymers used on a large scale and commonly known as "plastics" (polyethylene, polypropylene, polyvinyl chloride, polystyrene, among others), has a large part of its production based on petroleum, while its excessive use and improper disposal generate millions of tons of microplastics that negatively impact the environment and the lives of countless people. NPs, in turn, are often obtained by the use of expensive and harmful reagents, which can generate problematic consequences during the disposal of byproducts, while some of the NCPs, in addition to being generated directly from the mixture of the two materials mentioned, can also present high production costs and negative impacts in terms of energy demand and reagents, depending on the chosen preparation route (GOUR; JAIN, 2019; STANTON et al., 2020; LAW; NARAYAN, 2021; KANWAL et al., 2022; YING et al., 2022).

The present study aims to generate a comprehensive literature review on polymeric nanocomposites based on metal oxide nanoparticles, exploring the main methods developed to make them more sustainable. At the end of this review, it is expected to provide an in-depth understanding of the topic, helping students, researchers, producers of consumer goods and other interested parties to use this knowledge to make more informed decisions in the stages of choosing, obtaining, producing, consuming and disposing of these materials.

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METHODOLOGY

The scientific literature that supports this text was gathered, studied, and compiled between July 2023 and 2024, as part of the development of the introduction to nanotechnological research work carried out by the bachelor's student mentioned as the first author of this article, under the guidance and supervision of the co-author professors and researchers. The researches were carried out using databases that offer comprehensive and specific information, with emphasis on those whose topicality, credibility and relevance in the areas of Chemistry, Natural Sciences, Exact Sciences, Earth Sciences and, more specifically, Technology and Materials Engineering, are proven. Namely: Google Scholar, Scopus, Royal Society of Chemistry, PubMed/NCBI, Springer Nature, Science Direct, and Web of Science. For reasons of technical and didactic adequacy, only works published in Portuguese or English were reviewed.

The descriptors used in the research were: nanoparticle synthesis, sustainability, sustainable nanoparticle synthesis, polymer synthesis, sustainable polymer synthesis, nanocomposites, polymer nanocomposites, sustainable polymer nanocomposites, metal oxide nanocomposites, metal oxide nanoparticles, nanoparticles green synthesis, green synthesis of metal oxide nanoparticles, sustainable polymers, sustainable nanoparticles and sustainable polymer nanocomposites, in English and/or Portuguese. In addition, the names of each of the metal oxides, polymers and polymeric nanocomposites addressed were analyzed individually for a more precise detail, when necessary. As for the temporal placement, priority was given to publications with the greatest possible modernity, including books and articles from the last fifteen years, to ensure that the information is up to date. However, some classic books and studies—from earlier decades—have been mentioned to provide historical context and highlight pioneering terms and events.

The contents found were filtered based on their relevance to the specific topic, prioritizing publications from the highest impact journals in the areas of nanotechnology and polymer science. The maintenance of the accessible and direct writing style legitimizes the protagonism of an undergraduate student who in fact signified his studies through active methodologies, but also aimed to make the review more manageable, without compromising the quality of the coverage of fundamental concepts, relevant aspects, innovations and future challenges. Thus, it is intended not only to synthesize and recirculate technical contributions, but also to arouse the interest of those who are not from the academic environment, promoting the socialization and dissemination of knowledge, and contributing to the education and popularization of science and technology.

RESULTS AND DISCUSSION

The viability of polymeric nanocomposites reinforced by metal oxides depends on the final properties of the material and the sustainability of its production chain. Therefore, it is essential to review the properties and limitations of the synthesis and application of metal oxide nanoparticles and the polymers that contain them. Although this work does not specifically deal with post-consumer management, it is essential to recognize that the form of use and final destination of polymeric nanocomposites and their components, such as metal oxides, have significant impacts on the environment and society. Products such as packaging, clothing, toys, utensils, and electronics, which frequently use these materials, can generate adverse effects if not properly handled and discarded. It is crucial that society and producers adopt responsible practices that minimize environmental and socioeconomic impacts. This includes promoting recycling, sustainable use, and innovation in disposal methods. Awareness and education about the proper disposal of these materials are important steps to reduce pollution and promote sustainability. In addition, nanotechnology and plastics should not be seen in a negative light. While there are legitimate concerns about their environmental impact, both have the potential to contribute significantly to technological development and improved quality of life. The key lies in finding a balance between the benefits these materials offer and the responsibility with which they are used and disposed of.

METAL OXIDE NANOPARTICLES (NPsOMs)

Metal oxides (MOs) are chemical compounds formed by combining metals with oxygen, resulting in materials with a wide range of physical and chemical properties arising from the chemical interactions between atoms and their varied crystalline structures. These compounds are critical in a variety of industries, including electronics, construction, medicine, and chemistry, due to their stability, strength, and reactivity. Among the most wellknown metal oxides are titanium dioxide $(TiO₂)$, used as a pigment and in sunscreens, aluminum oxide (A_2O_3) , essential in the manufacture of ceramics and abrasives, and iron oxides (FeO, Fe₂O₃, Fe₃O₄), which play a crucial role in catalytic processes and in the production of magnetic materials (GRILLI, 2020).

Metal oxide nanoparticles (NPsOMs) have unique and distinct properties from their traditional counterparts (bulk) due to their small size and high relative surface area. These differences allow for a wide range of new technological and medical applications, but they also require special care regarding toxicity and environmental impact. NPsOMs have a

much larger surface area than macro and micrometer particles, which increases their surface reactivity, making them more effective in catalytic and adsorbent applications compared to traditional metal oxides. In addition, the reduced size of nanoparticles can result in different electronic and optical properties, including quantum effects that are not observed in bulk materials, giving them greater variability in light absorption and emission, useful in optical sensors and photonic devices. In terms of mechanical properties, some NPsOMs may have altered strength and hardness due to the higher proportion of surface atoms, while traditional OMs have more stable and predictable mechanical properties (RALLINI; KENNY, 2017; GRILLI, 2020; KHAN et al., 2023).

The thermal properties also differ; The thermal conductivity of nanoparticles can be reduced due to phonon scattering. NPsOMs can interact distinctly with biological systems, exhibiting antibacterial properties and potential for use in biomedical applications, but also greater toxicity in certain contexts, in contrast to traditional metal oxides, which are generally more biocompatible and less reactive. These differences are reflected in the applications: the particles of OMs of smaller size are widely used as catalysts, sensors, electronic devices and in diagnostic medicine, while the clusters, concentrations and sizes larger than the nanoscale are observed mainly in ceramics, coatings, refractory materials, implants and prostheses (RALLINI; KENNY, 2017; GRILLI, 2020; KHAN et al., 2023).

In the context of polymeric nanocomposites, NPsOMs offer a number of advantages, improving the matrix's mechanical, thermal, barrier, optical and electrical properties, and enabling the creation of new, lighter, more durable and functional materials for a variety of industrial and commercial applications. Thus, these particles have been widely used in the modern world and have several possibilities of application (FU et al., 2019).

Examples of NPsOMs, their properties of interest and some common uses are summarized in Chart 1.

Fonte: Adaptado de ALAM; KUMAR; PARK, 2022; CHAKRABORTY et al., 2022; DA ROCHA et al., 2024a; DA ROCHA et al., 2024b; SAYYED et al., 2023; ROCA et al., 2023; ALI et al., 2016; BOEY; MANIAM; HAMID, 2011; CHO; TOMAS DA ROCHA; JUNG, 2024; DE CASTRO et al., 2017; GRIGORE et al., 2016; GUDKOV et al., 2022; HABTE et al., 2019; HAIDER; JAMEEL; AL-HUSSAINI, 2019; HASSANPOUR et al., 2018; HAYES et al., 2020; KOŁODZIEJCZAK-RADZIMSKA; JESIONOWSKI, 2014; LEE; LALDAWNGLIANA; TIWARI, 2012; MIRI et al., 2018; MU et al., 2017; PROKAEWA et al., 2022; RASHAD, 2013; ROY et al., 2013; SAQIB et al., 2019; SOLTAN; SERRY, 2011; TEMPLETON et al., 2001; WARKAR, 2022; ZIENTAL et al., 2020.

The information contained in Chart 1 allows us to broadly understand how essential NPsOMs are today, given their applications in practically all areas relevant to life in the twenty-first century: urban construction, metallurgical, medicine, electronics, agriculture, energy production, industrial production and scientific research. Therefore, it is not surprising that the production and production of such materials has reached industrial scales in the last century - something that has brought with it a large number of environmental and social problems given the abundance of methods tested and

disseminated over the years, aiming at technological advancement and profit, without necessarily validating the socio-environmental aspect. Many of the aforementioned materials are found in natural deposits on the planet, such as iron oxides in the form of magnetite, while others need to be generated chemically, such as CaO, which is found in the form of CaCO3 in calcite. There are numerous ways to naturally produce or obtain OMs, depending on the availability of natural resources, labor, technical apparatus, chemical reagents, energy matrix, and, finally, of course, the choice of the final characteristics desired in the particle. In any case, whether synthetic or not, the ways of exploring the benefits of NPsOMs, as well as those of NPs in general, can be didactically grouped into three blocks: physical, chemical, and biological processes (NAM; LUONG, 2019; IJAZ et al., 2020).

Physical processes consist of Top-Down methods that use mechanical, electrical, and thermal stresses for the removal and reduction of excess material and impurities resulting in the creation of NPs. Some of the most common are based on laser ablation, electric arcs, spray pyrolysis, ball mills, transformation and subsequent condensation of steam and gas, electrical discharge in pulses, and lithography. For example, nanotitanias, widely exploited for their photocatalytic properties and, in cosmetics, for UV protection, are commonly produced through ball mills, a physical process (THEIVASANTHI, 2017; JAMKHANDE et al., 2019; IJAZ et al., 2020; PATIL et al., 2021).

In contrast, chemical processes consist of Bottom-Up approaches to NP formation by use of chemical interactions. Examples of these include chemical reduction, sonochemical synthesis, microemulsion, photochemistry, electrochemistry, pyrolysis, microwaves, solvothermic synthesis, and coprecipitation. Namely, quicklime (CaO) can be produced by the thermochemical decomposition of CaCO3, a form of chemical reduction. Biological processes also consist of Bottom-Up methods of forming NPs by using biological raw materials and/or natural chemical processes of certain organisms, which stand out for generating a smaller amount of harmful by-products than often generating biodegradable waste. Examples are: use of plants and their extracts, use of bacteria, fungi, algae, enzymes, biomolecules and microorganisms in general. Nanoparticles of various metal oxides, such as aluminum, cobalt, copper, iron, manganese, nickel, silver, titanium, zinc, among others, can be obtained from plant extracts by green biological processes of oxidation-reduction (DHAND et al., 2015; NAM; LUON, 2019; IJAZ et al, 2020; CHAKRABORTY et al., 2022).

Physical and chemical processes commonly prioritize cost and the ratio of the

amount of NPs created over time, completely neglecting the possible damage that such methods can cause to the contemporary industrial production scale. The mass generation of CaO from CaCO3, for example, is a major contributor to air pollution due to CO2 supersaturation, since chemical reduction generates this component as a byproduct. On the other hand, biological processes, as they are more aligned with the principles of green chemistry, represent a significant advance, being more sustainable and environmentally friendly (FEBRIATNA; DARMANTO; JUANGSA, 2023).

Of the three groups of methods mentioned, biological processes present, in general, greater effectiveness in terms of generating NPs by green chemistry. In fact, biological processes are generally considered the most effective in terms of green chemistry because they use biological raw materials such as plants, bacteria, fungi, and other microorganisms to synthesize NPs. These methods tend to be more sustainable and environmentally friendly since they use natural processes and often result in biodegradable byproducts. For example, using plant extracts to produce NPs of CuO minimizes the use of toxic reagents and reduces environmental impact. However, physical processes become "greener" when they are adapted to reduce energy consumption. It is also possible to carry out some chemical processes in a relatively ecological way, as long as the reagents are not potentially toxic or generate waste that is harmful to human health and the environment. Green chemistry focuses on the reduction of hazardous substances and sustainability, while some chemical methods attempt to adhere to these principles, they are considered intrinsically ecological (IJAZ et al., 2020; ÁLVAREZ-CHIMAL; ÁNGEL ARENAS-ALATORRE, 2023).

Green methods for the production of NPs represent a significant advance in nanotechnology, standing out for their sustainability and minimizing environmental impact. These methods use biological and chemical processes that align with the principles of green chemistry, seeking to reduce or eliminate the use of hazardous substances, decrease waste generation, and increase energy efficiency. The processes known as biogenic synthesis involve the use of living organisms or their extracts to synthesize NPs. Plants, bacteria, fungi, algae, and enzymes are commonly employed due to their natural ability to reduce metal ions to nanoparticles. This method not only reduces environmental impact, but is also energy-efficient and generates by-products that are often biodegradable (MIRI et al., 2018; GOUR; JAIN, 2019; IJAZ et al., 2020; SHANKER; HUSSAIN, 2022).

While traditional chemical methods often require the use of toxic reagents and extreme reaction conditions, green chemistry offers alternatives that align with the principles

of sustainability. Examples include chemical reduction, which can be performed with less harmful reagents and under milder conditions, and solvothermic synthesis, where non-toxic solvents are employed to minimize environmental impacts. In addition, techniques such as coprecipitation and sonochemical synthesis can be adapted to become more sustainable by using biodegradable surfactants and controlling reaction conditions in a way that reduces waste generation (DUAN; WANG; LI, 2015; SHANKER; HUSSAIN, 2022).

Nanoparticles are widely used in various industrial and medical applications due to their unique physical and chemical properties. However, these uses also raise concerns about potential environmental and human health impacts. PNs are employed in diagnostics, targeted therapies, controlled drug release, and biomedical imaging. For example, titanium dioxide nanoparticles are used in contrast agents for MRI and in phototherapy. In addition, they are applied in catalysts, sensors, electronics, cosmetics and as additives in building materials. Silver nanoparticles, for example, are valued for their antimicrobial properties and are safely used in fabrics and coatings. However, despite the benefits, some NPs can be harmful, in certain concentrations and sizes. Studies indicate that heavy metal nanoparticles can induce cytotoxicity and genotoxicity, resulting in cell damage and genetic mutations; and prolonged exposure can lead to adverse health effects, such as lung inflammation and cardiovascular problems (IRAVANI et al., 2014; OU et al., 2016; GOTTARDO et al., 2021).

Improper disposal of NPs can lead to environmental contamination. When released into the environment, NPs can persist in soil and water, affecting aquatic and terrestrial organisms. To circumvent their possible adverse effects, many NPs are designed to be bioinert, i.e., not biologically reactive, which can prolong their stay in the environment and potentially cause bioaccumulation in the food chain. To mitigate the impacts as much as possible, it is crucial not only to think about synthesis, but also to develop effective strategies for the disposal and recycling of NPs. Methods such as advanced filtration and photodegradation can be employed to remove NPs from industrial effluents. In addition, strict regulation and the implementation of responsible manufacturing practices are essential to minimize the risks associated with the use and disposal of nanoparticles (GOTTARDO et al., 2021; KUMARI et al., 2023; SINGH et al., 2023).

Therefore, it is possible to observe, through the increasing use of metal oxide nanoparticles (NPsOMs), the crucial role of these particles in various sectors due to their unique properties. However, the production and application of these NPs still face significant challenges, such as environmental impacts and health risks related to their

toxicity and persistence. The adoption of green methods for the production of nanoparticles and the implementation of safe disposal practices are essential to ensure sustainability in Nanotechnology. The environmental concerns and toxicological aspects associated with these materials are summarized, reinforcing the need for an always conscious and informed approach. In addition, several nanometric materials have been studied, including their potential to remedy environmental problems and combat climate change (SHANKER; HUSSAIN, 2022; CHAUSALI; SAXENA; PRASAD, 2023; SINGH et al., 2023). Thus, the time has come to propose the replacement of many of the conventional methods with nanomaterial-based technologies, balancing scientific advancement with environmental preservation and public health, using appropriate regulations and responsible manufacturing practices to maximize the benefits of nanotechnology in a safe and environmentally friendly way.

POLYMERS

The environmental and socio-economic challenges related to polymers are intrinsically linked to the properties that make them extremely valuable to the industry. Especially synthetic ones, they stand out for their very high chemical and mechanical resistance, malleability, versatility and, above all, for their very low degradability and bioinertia. These characteristics make them widely used in a variety of industrial applications, including coatings, food and object storage, and in various industrial processes. However, the same qualities that give polymers their industrial advantages also pose significant challenges. The low degradability of synthetic polymers implies that once discarded, they remain in the environment for long periods, accumulating in landfills, oceans, and other ecosystems. This persistence contributes to environmental pollution and affects the quality of natural habitats. The low reactivity of polymers with most chemical and biological compounds is a contributing factor to their durability, but also to their environmental problems. The inability of polymers to be easily broken down by natural processes means that they can be ingested by living organisms. When plants and animals internalize (via respiration or ingestion, for example) polymeric particles, they can accumulate in the food chain, leading to harmful effects on human health such as inflammation, infections, digestive disorders, gastrointestinal changes, metabolic and hormonal changes. In addition, the presence of nano and micro and macroplastics can alter the quality of air, soil and water, also affecting fauna, flora and biodiversity. Therefore, despite their value and utility, polymers present significant challenges that highlight the

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urgent need for effective strategies for waste management, development of their more sustainable versions, and awareness of their use and disposal. The adoption of more responsible and innovative practices is essential to mitigate the potential adverse consequences associated with these materials and promote a more balanced and safe approach (MANO; MENDES, 1999; MANO, 2000; BRO; DAYS; OLIVEIRA, 2004; Handbook of Polymer and Ceramic Nanotechnology, 2021; Advanced Polymer Nanocomposites, 2022; AMARAKOON et al., 2022).

To understand the importance of green polymer synthesis processes, it is necessary to analyze the process of creating them from the extraction of the raw material to the creation of the final product. Regarding the obtaining of the raw material, it is noted that more than 99% of the plastics used commercially are derived from monomers obtained from fossil fuels, the most common being polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET) and their respective derivatives. Therefore, all the problems associated with the extraction of fossil fuels also apply to common plastics, including marine pollution, ecosystem disturbance and air pollution - problems that add to those mentioned in the previous paragraph (SEN; PUSKAS, 2015; SON; SANFELICE, 2018; RHODES, 2018; WILLIAMS; RANGEL-BUITRAGO, 2022).

The synthesis of materials that we know as plastics, but also of rubbers and fibers, occurs through smaller molecules called monomers, which react and covalently bind to form polymers. To this end, different mechanisms - addition, condensation, coordination - can be conducted, under different reaction conditions, including solution and mass polymerization. Several industrial polymer production processes are logistically unsustainable, involving the use of monomers derived from fossil fuels, high energy consumption, use of toxic organic solvents, and inadequate waste disposal practices. The subsequent processing for the functionalization of polymeric materials is also carried out in an unsustainable way in some of the usual methodologies, directly contributing to the generation of a large amount of tailings that disturb the balance of natural ecosystems and negatively affect people's lives (MANO; DAYS; OLIVEIRA, 2004; GEYER, 2020; SCHWAB et al., 2024).

On the other hand, it is important to be aware that several natural biological processes use polymerization to create organic molecules essential for the functioning of life, such as the production of cellulose in plants and DNA in all cellular beings on the planet. In addition, several polymers, even if synthetic, are not so socio-environmentally harmful since: they are produced from renewable sources, such as biomass, which reduces dependence on fossil fuels and reduces the carbon footprint; or they are biodegradable,

decomposing faster and safer in the environment; or they can be recycled and reused, reducing the need for new raw materials and minimizing waste generation; or, even, they are formulated to somehow have less toxicity, both during their production and disposal, reducing the risk of environmental contamination and damage to human health. Therefore, it is noted that polymers themselves are not a problem, and that there are ways to generate and consume them in harmony with the environment (AVÉROUS; POLLET, 2012; GUILLET, 2012; GEYER, 2020; SALEH, 2021; KANWAL et al., 2022).

The inappropriate disposal of polymeric materials after use, especially plastics, represents one of the greatest challenges associated with the use of polymers (especially synthesized from fossil sources) in contemporary society. The lack of public awareness about the risks of improper disposal, the absence of industrial incentives to prioritize environmental health, and the inherent properties of most plastics converge to create one of the greatest challenges in waste management in the modern era. Given that the socialization of scientific education and political and industrial reform with a focus on collective and planetary health are outside the scope of this article, the present discussion is restricted to exploring strategies around polymer-based nanomaterials with minimized environmental impact (KRISHNAMOORTI; VAIA, 2007; GUILLET, 2012; KHALAF, 2016; FU et al., 2019; STANTON et al., 2020; AMARAKOON et al., 2022; KANWAL et al., 2022).

The problems related to conventional plastic materials are a consequence of both the raw materials used and their ways of obtaining them, as well as the practices of reckless polymerization, processing, use and disposal. In this context, the need to adopt more sustainable synthesis, application, and disposal techniques for polymers, blends, and composites becomes evident. Considering that the beneficial properties of conventional plastics are precisely the ones that contribute the most to bioaccumulation and environmental pollution, it is imperative to develop new materials that can emulate or replace them, but with the added benefit of sustainability bias — something that has been achieved with some success through the development of green polymeric nanocomposites, as we will discuss below.

POLYMERIC NANOCOMPOSITES REINFORCED BY METAL OXIDES

Polymeric nanocomposites are materials composed of a polymeric matrix in which nanostructures are dispersed in order to improve their properties. These nanostructures can be represented by xxxxx, nanoparticles of metal oxides such as titanium, silver, copper, zinc, molybdenum, iron, aluminum, nickel, cobalt, manganese, vanadium and many others,

as mentioned earlier. Metal oxides can confer desirable properties to nanocomposites such as: mechanical strength, antimicrobial properties, UV absorption capacity, electrical conductivity, cathalactivity, photocatalyticity, thermal stability, structural reinforcement, adjustable optical properties, resistance to chemicals, anti-corrosive properties, biocompatibility, self-repair, surface hydrophobic characteristics, among others. However, it is critical to assess the potential risks associated with the use of these materials. It is important to consider the potential impacts on human health and the environment throughout the material's life cycle, from manufacturing to final disposal (AVÉROUS; POLLET, 2012; GUILLET, 2012; YIN; DENG, 2015; NASKAR; KEUM; BOEMAN, 2016; KHALAF, 2016; WRÓBLEWSKA-KREPSZTUL et al., 2018; WANG et al., 2020; DA ROCHA et al., 2024).

The properties of metal oxide-reinforced polymeric nanocomposites (NCPsOMs) result directly from the production methods and constituents used, the interactions between the polymer matrix and the nanoparticles, as well as the specific processing conditions. Given the current scenario, which advocates profit, it is not surprising that polymers with already well-established, but not at all sustainable, industrial plants are still frequently studied, valued and employed as matrices for the creation of NCPsOMs, which often contain toxic nanoparticles or equally unsustainable in terms of the route of production. This results in the production of environmentally harmful materials such as polyvinyl chloride (PVC) containing $TiO₂$ nanoparticles. Consequently, several studies indicate that some NCPsOMs should be avoided as they can pose significant environmental risks (LA ROSA, 2023; SARKER et al., 2023).

It is essential to know the main methods for the synthesis of polymeric nanocomposites reinforced with metal oxides, as each method offers specific advantages and meets different manufacturing requirements and properties of the final material, especially regarding performance, recyclability, and degradability. Direct mixing of the nanoparticles in the polymer matrix is a simple and efficient method for some applications, although it may not guarantee the desired uniformity. The sol-gel method allows the formation of a material with a fine and homogeneous structure from liquid precursors, being ideal for when high uniformity and control in the structure of the nanocomposite is required. Polymerization in nanoparticulate media integrates the nanoparticles during polymer formation, resulting in a polymer matrix with more uniform and performance-optimized distribution. Understanding these methods is crucial to select the most appropriate approach to achieve the desired properties and ensure the effectiveness of the

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nanocomposite for specific applications (LUAN et al., 2012; FAWAZ and MITTAL, 2014).

One of the most widely used methods for the formation of polymeric nanocomposites reinforced with metal oxides is mechanical mixing, which involves dispersing the nanoparticles directly into the polymer matrix through mechanical forces. In this process, the nanoparticles are dispersed in the polymer in their solid form, obtained by grinding, high-speed agitation or other similar methods. Although this method is relatively simple and scalable, the uniform distribution of nanoparticles can be challenging, and the effectiveness of reinforcement can vary (AKPAN et al., 2019).

Dispersion in solution offers precise control over the distribution of the nanoparticles in the polymer matrix. It starts with the dispersion of the nanoparticles in a suitable polymeric solution, and the choice of solvent is crucial to ensure good dispersion without affecting the properties of the polymer. Ensuring a homogeneous mixture is essential to avoid agglomeration of nanoparticles. The resulting solution is then deposited on an appropriate substrate, such as a mold, through techniques such as centrifugal coating or dipping. The solvent is then removed by evaporation to prevent the formation of agglomerates. However, maintaining dispersion stability can be challenging, especially for nanoparticles prone to agglomeration, and may require the use of stabilizing agents. Solvent selection is also critical to prevent polymer degradation, taking into account toxicity and volatility issues at industrial scales. In addition, achieving accurate morphology can be challenging and requires a deep understanding of the interactions between the nanoparticles and the polymer. Process scalability can be limited due to time, cost, and efficiency considerations, especially in large-scale deposition processes, which may require specialized equipment and specific operating conditions.

In situ polymerization methods represent a highly advantageous approach in the synthesis of polymeric nanocomposites reinforced by metal oxides. This strategy allows the direct formation of nanoparticles within the polymeric matrix during the polymerization process, offering an efficient integration of the components. In situ polymerization can be performed by several techniques, including solution, bulk, or emulsion polymerization. In these methods, the precursors of metal oxides are incorporated into the reaction mixture before polymerization occurs. This direct integration during polymer synthesis results in excellent dispersion of the nanoparticles in the matrix, promoting homogeneous distribution and often avoiding the need for additional mixing processes. This approach simplifies the manufacturing process and minimizes problems related to nanoparticle agglomeration and lack of adhesion to the polymer matrix. Thus, in situ polymerization methods stand out as a

promising option for the production of high-quality polymeric nanocomposites, with improved properties and potential for various applications (XU et al., 2023).

Physical deposition techniques, such as spray or electrophoretic deposition, are used to apply metal oxide nanoparticles to polymeric surfaces. These methods are useful for controlling the orientation or distribution of nanoparticles in films or coatings. In spray deposition, the nanoparticles are dispersed in a solution and then sprayed onto the polymer surface, forming a thin, uniform layer. Electrophoretic deposition uses an electric field to guide the nanoparticles towards the surface, allowing for controlled and efficient deposition, including directional orientation of the particles. However, both methods face challenges related to the optimization of deposition parameters, the adhesion of nanoparticles to the polymer surface, and coating uniformity, requiring a deep understanding of the interactions between the nanoparticles and the polymer (JEONG et al., 2016; GONZÁLEZ-CASTILLO et al., 2020).

In summary, the choice of the appropriate synthesis method for metal oxidereinforced polymeric nanocomposites depends on a number of factors, including the desired properties of the final material, the scale of production, and economic and environmental considerations. Each method presents unique advantages and challenges, and ongoing research in this area is focused on optimizing these processes to achieve composite materials with improved performance and reduced environmental impact.

In order to ratify and present in a concise and elucidative way the application of sustainable approaches in the development and use of polymeric nanocomposites reinforced with metal oxides, some of the works that contributed to the construction of the discussion are highlighted in Chart 2.

As can be seen in the Table, the development of polymeric nanocomposites reinforced by metal oxides has advanced significantly, offering innovative solutions for a wide range of applications. The growing concern with sustainability has driven research into greener and more efficient synthesis methods, which minimize environmental impacts and promote the circular economy. In this context, several studies have explored sustainable approaches to the manufacture of these materials, providing valuable insights into alternative techniques and methods that aim to reduce waste generation and improve process efficiency. Many works illustrate these strategies and their implications in the synthesis of polymeric nanocomposites.

Das, Parandhaman and Dey (2021) describe several methods of synthesis of nanocomposites (NCs) based on hydrogels using biomolecules. The polymers and nanoparticles (NPs) used for the synthesis of these NCs are, or can be, obtained at low cost from natural sources, such as biocellulose, polysaccharides and NPs of TiO₂ and ZnO. The NCs formed demonstrate a rate of generation of chemical waste similar to that found in natural polymerization processes, with negligible quantities. In addition, they note that such processes are carried out at ambient temperature and pressure conditions and use a considerably smaller amount of total energy, reducing the environmental impact and being useful for industrial processes. The synthesis methods discussed differ depending on the type of NC to be generated; all three types of synthesis (Mixture, Sol-Gel Method and Polymerization in Nanoparticulate Medium) are discussed, including the formation of a ZnO- (Sodium Alginate) nanocomposite film by the sol-gel method.

Ullah et al. (2021) developed and experimented with a technique for the creation of biocellulose organic-inorganic polymeric nanocomposites (NCPsOMs) with $TiO₂$ nanoparticles (NPs), using biomolecules from Gluconacetobacter hansenii. One of the limitations of the use of biopolymer-producing bacteria for the creation of NCs is that some NPs, such as $TiO₂$, have bactericidal activity that can hinder the creation of the material. In the experiment, the beat beating technique was used to break the cell wall of the bacteria, generating a solution composed of functional biomolecules. The NPs were then dispersed in the solution, and the in situ polymerization method was used. It is observed that, during the creation of the NPs, a non-sustainable chemical process was employed with reagents whose synthesis forms are unknown. However, the method of preparing the solution of biomolecules generating the polymeric phase is sustainable, requiring only supply for the growth of bacteria and generating biodegradable organic waste (bacterial debris and byproducts of bacterial digestion). There is no current evidence that the use of TiO₂ NPs synthesized by green methods is unfeasible for the creation of the same NCPOM, indicating a possible green path for the production of biocellulose-TiO₂ NCPsOMs.

Mondal, Anweshan, and Purkait (2020) provide a comprehensive review on the green synthesis of nanoparticles (NPs) and nanocomposites (NCs) based on iron and iron oxides, highlighting that all the methods discussed are biological in nature. They explore how biological processes, rather than traditional chemicals, can be utilized to produce these materials, offering a more sustainable alternative. In contrast, Amel and Hanaa (2021) report a specific method for the synthesis of $Ni(OH)_2@Mn_3O_4$ using chia seed extract. Although the material described is not an organic-inorganic polymeric nanocomposite

(NCPOM), the green approach to creating nanoparticles is relevant. This is significant because the methods described for the production of green NPs can be applied in several techniques for creating NCPsOMs, providing sustainable alternatives for obtaining these materials.

James, Smith, and Williams (2021) and Alessandro, Rossi, and Bianchi (2020) discuss a variety of methods for polymer and biopolymer synthesis, with a particular focus on green routes. Both articles explore how these sustainable approaches can be applied in polymer production, highlighting the environmental benefits and feasibility of these techniques. Rbaa, El-Mahdi, and Boukili (2022) investigate the green synthesis of a polymer called COS-g-Glu, based on chitosan and glucose, using biomimetic reactions for its production. Although the polymer COS-g-Glu is not an organic-inorganic polymeric nanocomposite (NCPOM), the methods described for its synthesis are relevant. These processes demonstrate how polymer production can be carried out in a sustainable manner and, when combined with nanoparticles (NPs) obtained by green methods, have the potential to generate NCPsOMs that share these ecological properties.

Priyadarshi, Kumar, and Rhim (2022) explore a green method for the synthesis of an organic-inorganic polymeric nanocomposite (NCPOM) composed of carboxymethylcellulose (CMC) and ZnO, using Zn^{2+} ions for cross-linking. In the experiment, the polymer sodium carboxymethylcellulose (Na-CMC) was used to generate Zn^{2+} ions that performed the cross-linking between the polymers, reinforcing the structure of the hydrogel created. These ions were converted into $Zn(OH)_2$ from $Zn(NO_3)_2$. The $Zn(OH)_2$ molecules, subsequently heat treated, formed ZnO nanoparticles (NPs), resulting in a CMC-ZnO-Zn²⁺ nanocomposite hydrogel. This method has a significant advantage over previous and unsustainable methods for the formation of similar NCPOMs, as it eliminates the need for NaOH and alkaline media in the formation of ZnO NPs. This simplifies the process, making it more efficient and drastically reducing the generation of toxic waste.

The organic-inorganic polymeric nanocomposite (NaCoPOM) of ZnO-(Sodium Alginate) described by Das, Parandhaman and Dey (2021) and that of ZnO-CMC-Zn²⁺ described by Priyadarshi, Kumar and Rhim (2022) highlight an interesting feature provided by the insertion of nanoparticles (NPs) in a polymeric matrix: the cross-linking of polymeric filaments. Metal ions (in this case, Zn^{2+}) form perpendicular bonds between the parallel polymer chains, strengthening the structure and generating a robust scaffolding. This process results in large empty spaces within an amorphous gel structure, conferring macrometric properties such as high porosity, transparency, and elasticity (swelling

capacity). Both NCPsOMs demonstrate biomimetic and biocompatible properties due to their constituent parts, making them applicable in organic tissue-related contexts. In the study by Priyadarshi, Kumar and Rhim (2022), the developed NaCoPOM was directly applied in organic tissue growth and wound care techniques, in addition to acting as an antimicrobial agent. These properties highlight the material's great potential for use in the medicinal field.

Ullah, Kumar, and Rhim (2022) discuss the characteristics and applications of biocellulose-TiO₂ organic-inorganic polymeric nanocomposite (NaCoPOM), highlighting its thermo-physicochemical and antimicrobial properties. Compared to pure biocellulose, NaCoPOM demonstrates greater thermal stability, with an initial decomposition temperature 35°C higher (298°C for pure biocellulose and 333°C for NaCoPOM) and a final temperature 65°C higher (346°C for pure biocellulose and 411°C for NaCoPOM). TiO₂ nanoparticles, due to their high melting point, contribute to this higher thermal stability, since part of the heat is absorbed by NPs. In terms of mechanical properties, NaCoPOM has a higher Young's modulus (0.97 GPa versus 0.38 GPa) and a superior tensile strength (limit of 20.98 MPa versus 17.54 MPa) compared to pure polymer, allowing NaCoPOM to withstand greater stresses. The antimicrobial activity of NaCoPOM has also been observed against E. coli bacteria, showing efficacy in eliminating microorganisms. The $TiO₂$ NPs in NaCoPOM interact with bacterial components such as proteins, polysaccharides, and phospholipids, leading to the degradation and denaturation of these molecules, disrupting the cell membrane and resulting in the death of the bacteria (ULLAH, KUMAR, and RHIM, 2022).

Sadek, Ghoneim, and Azzam (2023) describe the use of a NaCoPOM composed of ZnO and CuO nanoparticles, highlighting the high reactivity of these NPs with single-celled biological bodies. NPs induce cell death through the interaction of $Cu²⁺$ ions, formed Cu surfaces, and generation of reactive oxygen species from ZnO ions. The polymeric matrix of poly(ethylene oxide) allows NaCoPOM to adhere to pipe walls, creating an internal coating that physically prevents the formation of biofilms and enables the continuous release of NPs to attack biological contaminants.

Saidi, Muthuraj, and Muthusamy (2022) develop and test a technique to improve the efficiency of solar cells using an electrolyte functionalized with a NaCoPOM of $Co₃O₄$ NPs dispersed in a P(VP-co-VAc) matrix. The technique involves sonochemical processing for the functionalization of NPs with desired sizes and their dispersion in the matrix. The study shows that NPs act as catalysts for the diffusion of triiodide ions through the polymer matrix, increasing the efficiency of solar cells.

Tajik, Asgarian, and Molaei (2023) explore the use of diverse organic-inorganic polymeric nanocomposites (NCPsOMs) as active agents for the detection of environmental pollutants in air, water, terrestrial, and food contexts. One study demonstrates the detection of hydrazine, a pollutant with ammonia-like characteristics, using a vitreous carbon cathode (GCE) modified with a polytiophene NaCoPOM and ZnO NPs. The active ingredient is based on the reaction of the NPs with the pollutant and on the electrochemical signal generated by the matrix, detected by the GCE. Another sensor based on $TiO₂$, polyaniline, and Au has also demonstrated the ability to detect hydrazine by a similar process.

Kausar (2021) conducts an in-depth review on the applications of green polymeric nanocomposites in energy storage. The article cites the use of conductive polymers, such as polyaniline and polythiophene, along with NPsOMs, such as NiO and Mn_2O_3 , for the creation of electrodes in supercapacitors, in addition to the combination of these metal oxides with cellulose for the formation of sustainable electrodes.

These studies range from the use of biomolecules for the formation of nanocomposites to the application of innovative methods that contribute to the creation of materials with lower environmental impact and improved properties. The review of the methods and results presented by these authors not only reveals the capabilities and challenges associated with each approach, but also highlights the transformative potential of sustainable techniques in the production of polymeric nanocomposites. By analyzing the contributions of each study, it is possible to better understand how these practices can be integrated and optimized to achieve significant advances in the area.

CONCLUSIONS

After investigating the sustainable approaches applied to polymeric nanocomposites reinforced by metal oxides, this study highlights their feasibility and growing importance in both academic research and industrial applications. Throughout this review, the main methods of synthesis and incorporation of these nanoparticles in polymeric matrices were contemplated, with emphasis on routes that combine efficiency with sustainability principles. The literature analyzed shows that green synthesis methods of polymeric nanocomposites reinforced by metal oxides (NCPsOMs) are valid alternatives for forms of production of green nanocomposites from the creation of their constituent parts (NPs and polymers) to the creation and functionalization of the NCPOM itself.

Thus, it is ratified that polymeric nanocomposites developed with a focus on sustainable practices offer several advantages, including the reduction of environmental 1040

impact, the use of renewable resources and the minimization of toxic waste. In the studies addressed, materials with applications in areas such as medicine, sensors, energy storage, water treatment and solar panels were generated, using low-cost biomimetic techniques and low environmental damage. It is noted that the techniques already published are quite versatile and still demonstrate use for the creation of several new types of NCPsOMs. Despite the technical challenges identified, such as the compatibility between matrix and reinforcement, high production costs and the complexity of industrial scaling, advances in the area indicate a promising future. The application of the principles of green chemistry and the search for biodegradable and renewable raw materials are essential to expand the use of these materials.

The review also underscored the need for close collaboration between academia, industry, and regulatory bodies to overcome technical and economic hurdles, facilitating the wider adoption of sustainable nanocomposites. In addition, the continuous evaluation of the environmental and toxicological impacts of these materials is essential to ensure their safety and effectiveness, in addition to providing subsidies for the development of appropriate standards and legislation. It is concluded that the relatively new character of nanocomposite science is a reason for incentive to experiment with the creation of new NCs and NCPsOMs based on the analyzed techniques due to their green characters, demonstrating high potential for the dissemination of these techniques as substitutes or novel forms of production that can compete with current industrial processes that are highly unsustainable, such as the production of common plastics (PVA, PE, PET, PVC etc).

In conclusion, with the increasing demand for sustainable technologies, polymeric nanocomposites reinforced by metal oxides have enormous potential to become preferred materials in various industries, contributing significantly to technological innovation in an environmentally responsible manner. For this potential to be fully realized, a continuous effort in research, development and education will be necessary, promoting the integration of new technologies with practices that benefit both society and the environment.

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