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Microplastics from Plastic Waste as a Limitation of Sustainability of the Environment

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Abstract: The massive emergence of plastics has contributed to their widespread use in everyday life. Unfortunately, the lack of appropriate technologies for processing these materials has contributed to environmental pollution by plastic particles. This study investigated the possibility of obtaining nanoparticles from selected plastics such as polyethylene and polyethylene terephthalate. Polyethylene was obtained from plastic bag waste, and polyethylene terephthalate was from crushed plastic bottles of mineral water. The first stage of nanoparticle production was to grind the collected used plastic waste, i.e., plastic bags and plastic bottles, to the smallest possible size using a cutting mill. Next, the waste was ground in a planetary-ball mill and then homogenised in a homogeniser. The particle size distribution of the obtained particles for selected waste plastics was examined using the Dynamic Light Scattering (DLS) method. The objective of the work was achieved – as a result of the performed procedures, nanoparticles of waste plastics were obtained. The following average sizes for particular materials were obtained: plastic bottles (PET) 212.81 nm, plastic bags (PE) 208.14 nm, and smaller particles, e.g. 27.74 nm.

Keywords: nanoparticles, waste plastics, DLS, secondary plastic

1. Introduction

Nanotechnologies and nanoparticles and sustainable development

Nanotechnology is probably the most rapidly growing field of materials engineering that deals with structure at the nanometer level. Nanotechnology is defined as the fabrication of elements of matter and/or the formation of their morphology on a scale of 1 to 100 nm. This conventional metric range is often not confirmed in practice. Therefore, a second component of the definition of nanotechnology has been adopted. It refers to physicochemical phenomena and says that nanotechnology exploits unusual properties of a substance, appearing only after a critical size of grains or precipitates, layer thickness, or particle size is reached (Sutisna et al. 2017, Hamdan et al. 2023). Of course, the critical size of a given structural element varies with different physicochemical properties. Nevertheless, to follow the first criterion of nanotechnology definition, it should be 1 to 100 nm. Nanotechnology is an area of materials engineering that is characterised by the fact that the size and morphology of structural elements can have a greater effect on the properties of a substance than its chemical composition. This effect is often called the nanoscale effect (Ciuła et al. 2023, Gaska et al. 2023).

When considering issues related to the impact of nanotechnology on the environment, it should be emphasised that the growing interest in the use of various nanomaterials in technology, industry, medicine and everyday life results in an increase in their production and, consequently, in their emission to the environment (Grąz et al. 2023). Due to numerous reports on the negative impact of nanoparticles on microbial cells, plants (Mateos-Cardenas et al. 2021, Yin et al. 2021) and animals (Li et al. 2021), it is necessary to assess their impact on the environment (Schwaferts et al. 2019, Jeon et al. 2021, Materić et al. 2021). This is particularly important in the case of newly synthesised products with potential applications in industry or economy (Gaylarde et al. 2021).

In recent years, nanotechnology and its products, i.e., nanoparticles, have greatly interested scientists. Nanoparticles, however, do not only bring benefits but also certain risks, both for humans (Magrì et al. 2021, Morgana et al. 2021, Roshanzadeh et al. 2021), and the environment (Croxatto Vega et al. 2021, Matthews et al. 2021, Wang et al. 2021). Their small size and large surface-to-volume ratio allow them to pass through body barriers unnoticed by humans. The skin, lungs and digestive tract absorb them. Once inside the body, nanoparticles can circulate freely, interact with biological systems and even penetrate individual cells without phagocytosis (Stapleton 2021, Grąz et al. 2022).

Different types of nanoparticles can accumulate in lipid vesicles, fibroblasts, cell nuclei, mitochondria or macrophages. Their presence has been found in the hearts of human infants and adults (Roshanzadeh et al. 2021). Toxicological studies have shown that nanoparticles can be cytotoxic, neurotoxic, genotoxic or ecotoxic (Shen et al. 2019, Jemec Kokalj et al. 2021). Most contaminants that enter the body are destroyed or neutralised by macrophages, the body's defence cells. Unfortunately, nanoparticles are extremely vulnerable to this process (Alwaeli 2009). Although the mechanisms of nanoparticles' impact on the human body and the environment are not yet fully understood, and the current knowledge of nanoparticles' toxicity is still very poor, according to the European Commission's official position, the development of nanotechnology should not be hindered. Still, all efforts should be made to ensure that a comprehensive risk assessment accompanies the design of new nanomaterials (Kihara et al. 2021, Yang et al. 2021, El-Baz et al. 2023). Especially that nano products are not only light, dirt-resistant clothing, self-cleaning glass surfaces or modern regenerating and nourishing cosmetics, but also a chance to produce artificial nerve fibres, contrasting nanomarkers for non-invasive me-dynamic procedures or a breakthrough in the treatment of many diseases such as Alzheimer's disease, cancer, glaucoma etc. Among the many benefits, it is important to remember that nanoparticle exposure can become a serious risk. Given the rapid development of nanotechnology, it is crucial to develop risk assessment criteria that protect against potentially harmful effects due to the specific properties of nanoparticles (Allan et al. 2021, Kumar Das et al. 2021, Mofijur et al. 2021).

Adverse effects due to the presence of micro- and nanoplastics should be limited. One of the activities that undoubtedly contributes to reducing microplastic emissions to the environment is the recycling of plastic waste. As a result of recycling plastic waste, secondary raw materials that can be reused are obtained. Nanoplastics are used in the production of cosmetics, industrial abrasives, and in the pharmaceutical industry for drug delivery, as well as for 3D printing (Bencsik et al. 2018, Alimi et al. 2018, Li et al. 2021). With such a wide and varied use of micro- and nanoplastics, increasing the share of secondary raw materials in these production branches, e.g., in the cosmetics industry, would be beneficial. The use of appropriate methods of processing plastic waste, leading to obtaining secondary micro and nanoplastics with appropriate quality parameters, may contribute to increasing the interest and, as a result, greater use of secondary raw materials in these industries (Khoironi et al. 2019). This article presents the secondary nanomaterials obtained from plastic waste containing PET and PE. The research aimed to create plastic microparticles, a major global problem, to see if they can be made and to consider their innovative reuse in accordance with circular economy principles.

Methods of producing nanoparticles

Nanoparticles are not very complicated structures in terms of their physical structure, but the ways of making them are not easy or simple. Nowadays, many fields of science and technology are looking for ways to use nanoparticles to improve the properties of already-known substances and materials. For this reason, scientists are trying to create particles that meet their high requirements in terms of spatial structure and strength, as well as the simplicity of application of nanoparticles in selected areas of science. There are two main techniques for creating structures that are less than 100-200 nm in size. The primary technique for bringing a material down to this size is called "top-down". This process relies on the mechanical processing of the material to reduce the particle size by grinding, cutting, grinding, or by chemical reactions that cause the substance to break down. Mechanical grinding methods cannot go below 150 nm in size for plastics due to their physical characteristics. Nanopolymers will not always have all dimensions below 200 nm due to the difficulty of grinding such substances. Materials with crystalline grains can even be fragmented to sub-100 nm in any space. The top-down method is a multi-step process and requires a considerable amount of time to produce nanoparticles. Humans have developed mechanical processing of substances to achieve structures in the nanoscale range as an anthropogenical method to produce these objects (Mamatha et al. 2020, Ekrami et al. 2022).

Another method of obtaining nanoparticles comes "from nature" and is called the "bottom up" method. This method creates particles directly from their constituent parts through chemical and physicochemical reactions. The reactions and processes in the "bottom-up" method are the reverse of those in the "top-down" method.

Here, instead of destroying to form nanoparticles, they are built from scratch. The bottom-up method allows for the precise design of the particle size needed for selected applications. This method is widely used in biotechnology and pharmaceuticals to apply certain substances precisely to specific locations (Alwaeli M. et al. 2018). Grinding and comminution of substances are used to analyse macromolecular substances that cannot be produced in any other way than by simply po-sizing the object. Fabrication by building is aimed at obtaining engineered nanoparticles for selected applications. Metals, ferromagnetites, and carbon compounds are mainly fabricated.

This paper uses the top-down method as a counterpart to natural and anthropogenic nanoparticle generation processes in the environment. This method mimics the generation of real polymer nanoparticle contamination of air, soil, and water.

2. Materials and Methods

Methodology for the fabrication of polymer nanoparticles

The fabrication of nanoparticles is a very tedious and complex process due to the very small size of the individual particles. The experiments started with the fabrication of macroparticles, then microparticles and finally nanoparticles were obtained. Polyethylene was obtained from new plastic bags, and polyethylene terephthalate from PET bottles.

Grinding in the cutting mill

The first stage of nanoparticle production is grinding accumulated material in the form of bottles and foil bags into the smallest possible forms using a knife mill (T 17 typ. M). The mechanism of the knife mill is to cut the material into smaller pieces with the help of attached blades. These blades have a counter blade which blocks the material, allowing it to be ground. This method makes it possible to achieve objects on the level of a few micrometres. However, the lack of tightness of the collection container results in creating a molecular cloud in the room and high air pollution with micro- and nanoparticles that can be created in this process.

Ball mill grinding

The next stage of comminution of the structures was grinding in a planetary ball mill Pulverisette 5. The principle of the planetary ball mill is based on the circular motion and the centrifugal force acting inside the grinding bowl. The grinding bowl is made of agate and 25 grinding balls with a diameter of 5 mm. The final material from the cutting mill was transferred in dry form to the grinding bowl. The grinding took one minute at 400 rpm. The resulting particles were transferred into sealed test tubes with a stopper using a spatula.

Homogenisation shredding

The last grinding stage was homogenisation grinding, which was used to break the flocculates formed after grinding in the ball mill. Homogenisation was carried out in the presence of the surfactant sodium dodecyl sulfate (SDS). The surfactant assisted in disrupting the nanoparticle phloem to extract individual particles. The homogeniser (Undrive x 1000D) was operated with a double knife at 32500 rpm.

Filtering

As the last process before the qualitative analysis of the obtained suspension, liquid filtering was performed to separate the nano- and microstructures. For this purpose, syringe filters with a pore diameter of 200 nm were used. The solution of nanoparticles thus obtained in distilled water was subjected to particle size distribution measurements in a DLS analyser.

Particle size measurement by DLS

The DLS (Dynamic Light Scattering) method is an analytical method based on dynamic light scattering. It allows us to measure particles in the 0.5-10000 nm range. The laser beam incident on the sample interacts with it and produces scattered radiation, which is then collected by the detector. Measurements with this method do not cause damage to the sample or structural changes in the sample. DLS is most commonly used to measure the size of particles in the liquid phase. In this study, each solution was made prior to analysis, allowing for the most accurate representation of sample content. The particle size distribution was determined using Malvern's DLS Zetasizer Nano Zs analyser. A total of 10 measurements were taken for each test material. The measurements were carried out at 25°C, using distilled water as a scattering phase, at an angle of 173° and a wavelength of 633 nm. Other measurement parameters: viscosity 0.887 cP, refractive index RI = 1.330.

3. Results and Discussion

By analysing the results obtained in individual measurements and comparing them to each other, a simple correlation can be drawn that the chosen sample preparation method was suitable for this type of study. Data obtained during DLS analysis of poly(ethylene terephthalate) and polyethylene show how little the individual measurement results differ from each other. The averages of the measurements for the two selected polymers are similar to each other. The difference between the average values is less than 20 nanometers, which indicates a very accurate qualitative analysis of the tested samples.

The analysis results using the Dynamic Light Scattering technique are shown in Table 1 for PET.

Table 1. Particle size distribution for PET

Poly (ethylene terephthalate)					
Peak 1 [nm]	Percent of area 1 [%]	Peak 2 [nm]	Percent of area 2 [%]	Peak 3 [nm]	Percent of area 3 [%]
208.3	100	0	0	0	0
202.3	100	0	0	0	0
204.0	100	0	0	0	0
203.9	100	0	0	0	0
224.8	100	0	0	0	0
213.4	100	0	0	0	0
223.6	97.4	30.5	2.6	0	0
220.6	100	0	0	0	0
223.4	98.7	24.98	1.3	0	0
221.8	100	0	0	0	0

Another very important aspect shown in Figures 1 and 2 is the distribution of individual peaks. It is very close, and only a few peaks fall outside the average area range. It suggests a homogeneous preparation of all samples for testing, and peaks above 1000 and those below 100 nanometers represent only a small percentage of the obtained results without constituting a sample base.

Figure 1 shows the distribution of the peaks for individual samples containing PET.

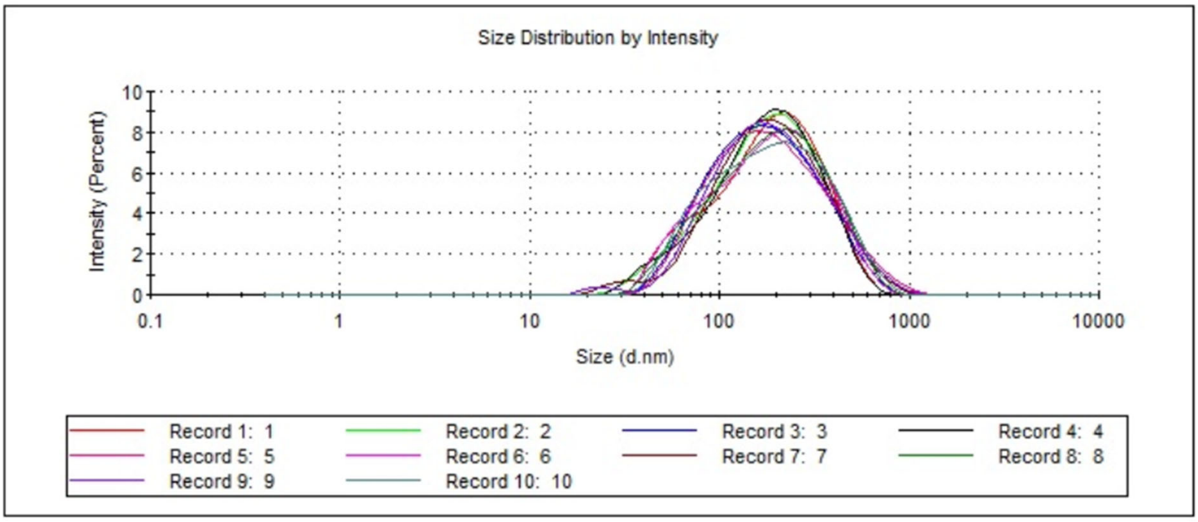

Fig. 1. Distribution of the peaks for individual samples containing PET

The average particle size values obtained are between 177 and 269 nanometers for the two selected polymers. The values obtained during this study support the belief that long time and exposure to degrading agents are not necessarily needed to produce nanostructures. Still, mechanical processing is sufficient to obtain nano-sized structures.

The analysis results using the Dynamic Light Scattering technique are shown in Table 2 for PE.

Figure 2 shows the distribution of the peaks for individual samples containing PE.

Table 2. Particle size distribution for PE

Polyethylene					
Peak 1 [nm]	Percent of area 1 [%]	Peak 2 [nm]	Percent of area 2 [%]	Peak 3 [nm]	Percent of area 3 [%]
184.7	97.3	5268	2.7	0	0
202.4	95.6	4151	4.4	0	0
231.0	97.6	3946	2.4	0	0
185.6	95.1	4462	4.9	0	0
269.9	100	0	0	0	0
182.6	97.2	4874	2.8	0	0
177.4	94.7	4645	5.3	0	0
204.1	97.9	4045	2.1	0	0
219.4	100	0	0	0	0
197.3	97.1	4724	2.2	10.21	0.7

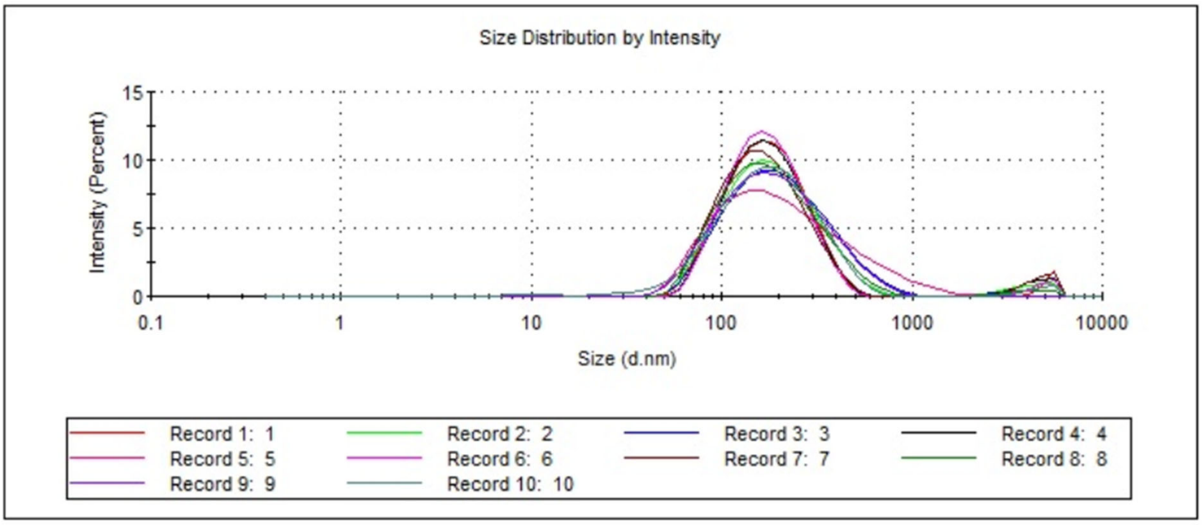

Fig. 2. Distribution of the peaks for individual samples containing PE

The developed method allowed the obtaining of secondary microplastics in a controlled manner, which can be used as intermediates for further use. It is estimated that, depending on the type of plastic, from 21% to 100% of the obtained secondary material can replace the primary material, covering 11% to 17% of the total material requirement (Gronba-Chyła et al. 2022, Klotz et al. 2022). Much research into determining the quality of recycled plastics has focused on examining the various pollutants present. However, it is extremely important to assess the loss of technical functionality of recycled plastics properly (Demets et al. 2021). It will allow us to determine the application paths of this type of material. Literature sources (Shamsuyeva & Endres 2021, Vasiliev et al. 2018) show that mechanical recycling is the most highly developed recycling approach in terms of industrial feasibility. This approach enables the development of plastic recyclates of various quality levels. The presented method does not define the technical parameters of the obtained nanoparticles, including the quality parameters, but it allows us to get them quite easily. A significant advantage of this method is its repeatability in terms of the size of the obtained particles. Obtaining nanoplastics in the form of nanoemulsions may contribute to increasing their use in the production of personal care products or other industries.

4. Conclusion

1. The production of nanoparticles is a time-consuming and complex process due to the very small size of individual particles. At the same time, particles smaller than 1 micrometre produced by plastic decomposition are hazardous to the environment and human health. Due to their size, these particles are not visible to the human eye, and they may travel long distances in an uncontrolled manner and affect plants, animals, and humans.

2. The aim of the study was achieved – nanoparticles of selected plastics were obtained by grinding and homogenisation. The following average sizes were obtained for particular materials: polyethylene terephthalate (PET) 212.81 nm and polyethylene (PE) 208.14 nm. It also produced single particles of size 24.98 nm (PET) and 95.1 nm.
3. The developed method allowed for obtaining secondary microplastics with repeatable sizes in a controlled way, which can be used as intermediates for further use. It's crucial to the circular economy.

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