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Constituents of Plastic Pellets and their Position in Waste Management from the Technological, Economic and Environmental Safety Aspects

Konstituenti plastičnog peleta i njihov položaj u upravljanju otpadom sa tehnološkog, ekonomskog i aspekta bezbednosti životne sredine

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Abstract: Although, according to the principle of the waste management hierarchy, recycling is only in the third place in the order of priorities, it is often presented to the public, unjustifiably, as a key solution that will contribute to the reduction of environmental pollution. However, almost all plastic, which represents a significant share of municipal solid waste, contains various toxic substances that, without elimination, find their way into the next production cycle. The suggestion is, justifiably, that plastics containing such contaminants should be labelled as non-recyclable materials. However, the question arises whether these are all contaminants or, in fact, at this level of production technology, constituents. This paper shows that toxic substances are present in plastic pellets for two reasons. The first is the production process of polymers and the raw materials used, and the second is an inadequate recycling process. Therefore, this paper goes one step further and proposes to limit, if not ban, the production and circulation of certain polymers.

Keywords: bisphenol A, brominated flame retardants, benzotriazole UV stabilizers, polycarbonates, recycling.

Sažetak: Iako je, prema načelu hijerarhije upravljanja otpadom, reciklaža tek na trećem mestu redosleda prioriteta, često se, neosnovano, u javnosti predstavlja kao ključno rešenje koje će doprineti redukciji zagađenja životne sredine. Međutim, gotovo sva plastika, koja predstavlja značajan udeo urbanog otpada, sadrži različite toksične materije koje, bez eliminacije, nalaze svoj put u narednom proizvodnom ciklusu. Predlog je, opravdano, da plastika koja sadrži takve kontaminate treba da nosi oznaku nereciklabilnih materijala. Međutim, postavlja se pitanje da li su to sve kontaminati ili, zapravo, na ovom stupnju tehnologije proizvodnje, konstituenti. Ovaj rad pokazuje da su toksične materije prisutne u plastičnom peletu iz dva razloga. Prvi je sam proizvodni proces polimera i sirovina koje se pritom upotrebljavaju, a drugi je neadekvatan proces reciklaže. Stoga, ovaj rad ide korak dalje i predlaže da se, ako ne i zabrani, onda ograniči proizvodnja i promet određenih polimera.

Ključne reči: Bisfenol A, bromovani usporivači plamena, Benzotriazol UV stabilizator, polikarbonati, reciklaža.

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INTRODUCTION

Since the invention of the first synthetic polymer in 1869 by John Wesley Hyatt, and the invention of Bakelite in 1907 by Leo Baekeland, plastics have become highly valuable in human lives. However, its massive overproduction has led to some major environmental concerns. Plastics or synthetic polymers are mainly produced of fossil fuels, combined with variety of additives in order to obtain specific characteristics. Several studies have shown that a myriad of additives is marked for potential use in plastic products, majority of with hazardous properties (Brosché et al., 2021; Dong et al., 2021; Fouyet et al., 2021). Still, the publicly available information about the size of the problem with toxins present in recycled plastic is very scarce, and the awareness about these chemicals and their health impacts is generally very low. Moreover, these substances represent a conditio sine qua non at today's level of plastic polymer production technology (Banaderakhshan et al., 2022). The most often used plastic recycling process is mechanical extrusion, resulting in plastic pellets (Figure 1), in which these toxic substances are not eliminated (Groover, 2012; Schyns & Shaver, 2020). In an IPEN study, Brosché et al. (2021) examined high density polyethylene (HDPE) pellets bought from twenty-four recycling facilities in twenty-three countries. They analysed pellets to determine the presence of eighteen substances, representing three types of toxic chemicals, namely: eleven brominated flame retardants, six benzotriazole UV stabilizers, and bisphenol A. They found out that none of the samples were free from all of the targeted chemicals, and twenty-one sample contained all three types of chemicals. More than half of the samples contained eleven or more chemicals, and seventeen samples contained five or more endocrine disrupting chemicals.

Figure 1. Recycled plastic pellets in Serbia (La Meccanica, 2018)

On the other hand, from the moment when manufacturers realized what was going to happen with the overproduction of plastic, they started investing in advertising campaigns about recycling as a solution to the problem, transferring the locus of control and responsibility for the environment to consumers (Nicholson & Leighton, 1942; Freinkel, 2011; Dauvergne, 2018; Najdić et al., 2019). This, among other things, have led to the opening of new markets for recycled plastics in many countries, as well as in Serbia, creating new opportunities for both small and large-scale recyclers. There are even small recycling units sold for domestic use (Latinović, 2018) as well as many YouTube tutorial promoting this activity. However, there is currently no transparency regarding what chemicals are added to plastics and consumers, downstream users, and recyclers have virtually no possibility to find out, nor, more importantly, they are legally obliged to do so (Lam et al., 2018). Recycling facilities therefore, not only have very limited abilities to exclude plastics containing toxic chemicals, but are also not incentivised to do so. Therefore, Brosché et al. (2021), with every right, suggested that “Plastic materials containing toxic chemicals should not be recycled but be considered non-circular”, and that “Manufacturers should phase out use of toxic chemicals in plastics, and make sure to disclose any toxic content to downstream users, consumers, recyclers and waste handlers” (Brosché et al., 2021). However, an equally justified questions arise such are “is this sufficient?”, and “what would this achieve in terms of environmental protection with already such a low share of recycled plastics?”.

1. METHODS

This paper tries to answer these questions, but also to go one step further. The work is interdisciplinary in its nature. Based on the literature review, the most significant toxic substances present in various polymers are discussed in Section 2, with a brief overview of the most significant health risks. In Section 3, the paper gives a brief overview of the most utilized sorting and recycling technologies in order to find the reasons for the presence of toxic substances in plastic pellets. Finally, the paper gives a critical review of the findings, and synthesizes them in a new perspective in Section 4. Finally, conclusion and proposals are given in the last Section.

2. HAZARDOUS CHEMICALS AND HEALTH CONCERNS

In the literature, three additives stand out as the most significant, according to their prevalence in the environment and the potential toxic effects they have on biota. These are brominated flame retardants, Bisphenol A, and benzotriazole UV stabilizers. Even though the name "additives" implies the addition of small amounts, these substances are actually constituents of plastics without which they would not have the appropriate characteristics.

2.1. Brominated Flame Retardants

Numerous types of brominated flame retardants (BFRs) have been applied in a series of commercial or industrial applications to satisfy fire safety standards and reduce the risks of fire. Examples can be building materials such as insulation, defoamers, various consumer products, etc. According to a 2020 market study conducted by IHS Consulting, the worldwide consumption of flame retardants amounts to more than 2.39 million tons, of which 17% of the share belongs to BRFs. The same study estimated that the consumption has grown substantially in the past 6 years, most in electronics industry, and that it will continue to grow at a global annualized rate of 2.7% until 2025 (IHS Consulting, 2020). The three traditional BFRs with the highest yield and the most widely used: polybrominated diphenyl ethers and biphenyls, hexabromocyclododecanes, and tetrabromobisphenol A (Dong et al., 2021). Considering their accumulation capacity, persistence and long-range transport potential, as well as their toxic effects, they pose a significant risk to the environment and human health. Currently, there are about 30 kinds of novel BFR (NBFR) which also showed neurotoxicity in experimental studies. Exposure to these NBFRs, as Dong et al. (2021) showed, can cause undesirable neurobehavior, especially during early neurodevelopment. The current neurotoxicity studies on these NBFRs mainly focus on NBFRs-induced developmental neurotoxicity, showing that NBFRs can damage the neuroendocrine system. NBFRs affect neural development mechanisms, including affecting thyroid/sex hormone levels, binding to thyroid hormone receptors and/or transporters, and receptor-mediated and non-receptor-mediated effects on sex steroids (Dong et al., 2021).

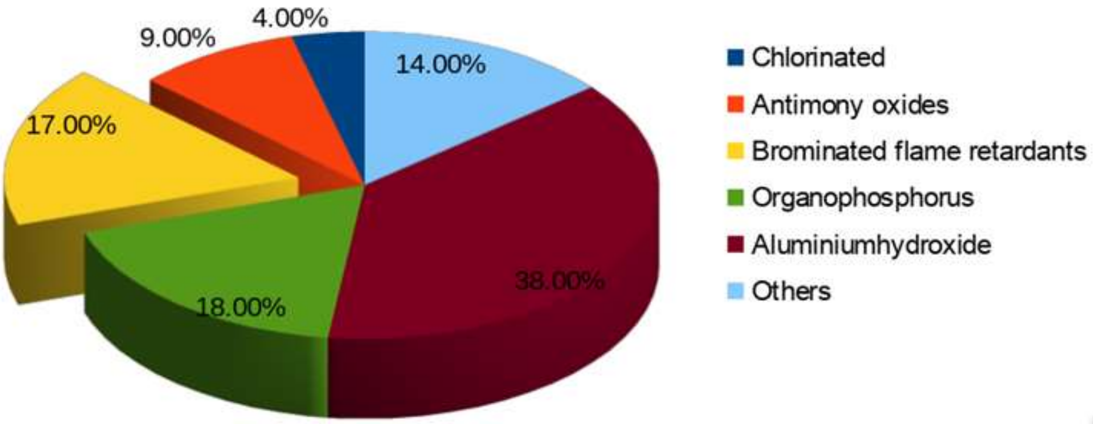

Figure 2. Global flame retardants consumption, by type, in 2019. Adapted from (IHS Consulting, 2019)

2.2. Bisphenol A

Bisphenol A (BPA) is a phenolic compound discovered in the late XIX century. It is a raw material for the production of high-temperature polycarbonate resins, and various other polymers (Tsai, 2006). It is therefore found in a wide range of products such as food and beverage containers, compact discs, personal protective equipment, sport equipment, dental products, and medical equipment, leading to multiple sources of exposure for the entire population (Suzuki et al., 2000; Fouyet et al., 2021). In humans, BPA is detected in the blood and urine (Genuis et al., 2012), but it is also found in the placenta and amniotic fluid (Fouyet et al., 2021). It has been listed as a substance of very high concern under the registration, evaluation, authorization and restriction of chemicals (REACh) legislation, first because of its reprotoxic properties and then because of its endocrine-disrupting properties. Fouyet et al. (2021), based on the experimental study, suggested that BPA, BPF, and BPS also induce toxicity in human placental cells. Its use has been limited and banned in baby bottles in Canada, in 2008, in France, in 2010, and in European Union, in 2011. In France, since January 2015, BPA has been forbidden in food and beverage packaging. These restrictions led manufacturers to use alternative bisphenols such as bisphenol F, and bisphenol S. According to the European Agency (ECHA), 187,000 tons of BPS-based thermal paper were placed on the EU market in 2019. By 2023, it is expected that 61% (or 307,000 tons) of all thermal paper in the EU will be BPS-based (Fouyet et al., 2021).

2.3. Benzotriazole UV Stabilizers

Benzotriazole UV stabilizers (BUVSs) are added to various polymers in order to prevent ultra-violet damage. In recent times, there is an emerging concern regarding the endocrine-disrupting effects of exposure to BUVSs (Sakuragi et al., 2021). Numerous BUVSs are extensively used as additives in various personal care products, including body lotions and sunscreens, as well as in plastic products to protect them from ultra-violet damage. However, BUVSs are reported to be highly lipophilic, bio accumulative and persistent in the environment (Wick et al., 2016). Moreover, these substances have been also detected in human breast milk (Kim et al., 2019). Findings, from the experimental study conducted by Sakuragi et al. (2021), suggest that BUVSs are emerging contaminants that are becoming ubiquitous in various environmental and aquatic biota matrices, and the concern regarding human exposure to this chemical series is increasing.

3. CURRENT PLASTIC RECYCLING TECHNOLOGY

Mechanical recycling is one of the most commonly used methods of plastic recycling (Serranti & Bonifazi, 2019). That method typically boils down to extruding mixed plastic waste and cutting the extrudate into pellets. That pellet, in the next production cycle, is extruded again, through different moulds, for the production of different parts or products. However, in order for the characteristics of the obtained part/product to have satisfactory properties, plastic waste must be adequately classified according to the type of plastic polymer, which represents a notable obstacle (Balaban, 2020).

3.1. Techniques for plastic waste separation

A mechanical process aimed to perform plastic waste recycling is based on the utilization of fast, accurate, and reliable tools and equipment specifically addressed to separate and recover single polymer streams, eliminating polluting elements (i.e., other polymers or other materials) present in the feed (Serranti & Bonifazi, 2019). Numerous techniques were developed. Table 1 gives an overview of the main contemporary separation techniques.

Unfortunately, each of the described techniques have specific drawbacks. For example, recycling of end-of-life black or dark colour plastics is hampered by the availability of suitable technology to sort them by polymer type (Serranti & Bonifazi, 2019). Near infrared spectroscopy sensor-based sorting, commonly adopted in plastic recycling plants, is unable to identify black or dark colour plastics, usually coloured with carbon black, due to their very low reflectance in this investigated spectral region. Another example is the case of biodegradable plastic, which can be mistaken for and mixed with conventional plastics, contaminating recyclate streams, as they cannot be recycled using conventional mechanical recycling techniques (Serranti & Bonifazi, 2019).

Table 1. Plastic waste separation technologies. Adapted from (Serranti & Bonifazi, 2019, pp. 16-28)

Gravity separation	Dry	Air classifier	Air classifiers use air as the medium to separate lighter materials from heavier ones. The waste stream enters the column with a raising current of air and lighter objects are blown upward whereas heavier ones are dropped down.
		Ballistic separator	Ballistic separation is based on a simple principle of the different movement characteristics of particles of different size, shape, and weight, spatially defined as 2D or 3D structures.
	Wet separation	Sink-float separation	Sink-float separation methods are based on the utilization of the different density properties of materials. Separation is based on the fact that when materials are introduced in a tank containing a fluid of a specific density, less dense materials will float and denser ones will sink.
		Jigging	A water stream is pulsed, or moved by pistons upward and downward, through the material bed. Particles are separated according to their densities, but also thanks to the systematic and repetitive applied pulsation, whose frequency and amplitude is strictly related to physical, morphological, and morphometrical attributes of materials.
		Hydro-cycloning	Hydrocycloning is a density sorting technology based on the centrifugal/centripetal forces and fluid resistance of different particles having different characteristics. Lighter fractions will be transported to the upper part of the cyclone, the heavier ones to the bottom.

Electrostatic separation		Electrostatic separation is usually applied when dielectric particles are handled. Dielectric particles, when electrostatically charged, can be separated according to their polarity charge.
Magnetic density separation		Magnetic density separation (MDS) is a density-based sorting process realized utilizing a “magnetic fluid” constituted by a liquid (i.e., water) and magnetic particles (i.e., iron oxide particles of about 10e20 nm) suspended in the liquid. Through a special magnetic field an artificial gravity is produced, as a magnetic force. Such a force varies exponentially in the vertical direction, and the effective density of the liquid also varies accordingly in the same direction. The result is that plastic particles) will float in the liquid at a level where the effective density is equal to their own density. In other words, particles characterized by different densities are suspended at different heights.
Flotation		Flotation works in a different way, from the sink and float process, in the sense that in a liquid medium, usually water, a “carrier” is introduced i.e., air bubbles, responsible to float hydrophobic particles that adhere to the bubbles with respect to the hydrophilic ones that sink.
Sensor-based sorting	Visible spectroscopy	Sorting in the visible range is mainly focused on the utilization of spectroscopic analytical techniques, performed in the wavelength range 400e700 nm, or on the adoption of digital imaging.
	Near infrared spectroscopy	Near infrared spectroscopy is probably the most utilized technology in plastic recycling. It is based on the collection of reflected spectra of polymers properly energized by a light source.
	Hyperspectral imaging	Hyperspectral imaging is a fast, and non-destructive technique able to collect both spectral and spatial information from an object.
	X-ray fluorescence	X-ray fluorescence is based on the detection of the emitted wave-lengths, as well as of the released energy, by a sample previously energized by X-ray whose atoms release energy generating an X-ray fluorescence radiation. The elements contained in the sample influence the emission both in terms of wavelengths and energy.
	Laser-induced breakdown spectroscopy	Laser-induced breakdown spectroscopy is an analytical technique based on the utilization of high-power laser pulse that performs an ablation of the sample to analyse, thus producing plasma plumes. The radiation produced by the ablated portion of the investigated material is then analysed by a CCD-based spectrometric device.
Auxiliary separation technologies	Magnetic separation	Magnetic separation is used to remove ferrous metal particles from plastics.
	Eddy current separation	Eddy current separation is based on the use of a high-speed magnetic rotor system and is used to remove nonferrous metals (i.e., aluminium and copper) from waste plastic streams. Due to the high speed of the rotor, an electric current, called Eddy current, is induced into conducting metals. The induced electric current produces a magnetic field, opposed by the field created by the rotor, repelling the conducting metals.

3.2. Production of plastic pellets

Extrusion is the leading method used in mechanical plastic recycling to produce pellets (regranulated material) from waste plastics. It is cheap, scalable, and solvent-free method, applicable to various polymers (Groover, 2012). Collected plastics are crushed, separated, washed, and shredded. Shredded plastic is fed to an extruder, in which, heat is used to induce thermal softening of the shredded plastic while rotating screws transport, amalgamate and propel the material through a die (Figure 3) (Groover, 2012).

The obtained extrudate is in the form of strings, which are then chopped into pellets and bagged for use. However, the thermal conduction and viscous shearing applied to polymers within an extruder leads to thermo-oxidative and shear-induced chain scission, chain branching or crosslinking of the material (Groover, 2012). The extent of the extrusion impact is dependable on the chemical characteristics of the polymer and the given process conditions. As Groover explains, “degradation can be controlled to some degree by choice of extrusion conditions. Temperature and screw speed have direct impacts on the process stability as well as the product quality” (Groover, 2012). Using excessive temperatures and screw speeds can accelerate chain scission and lead to the formation of unprocessable polymers (Schyns & Shaver, 2020). Finally, effluents from the process, carrying the described chemicals represent toxic waste which, in Serbia, goes directly into surface waters (Latinović, 2021).

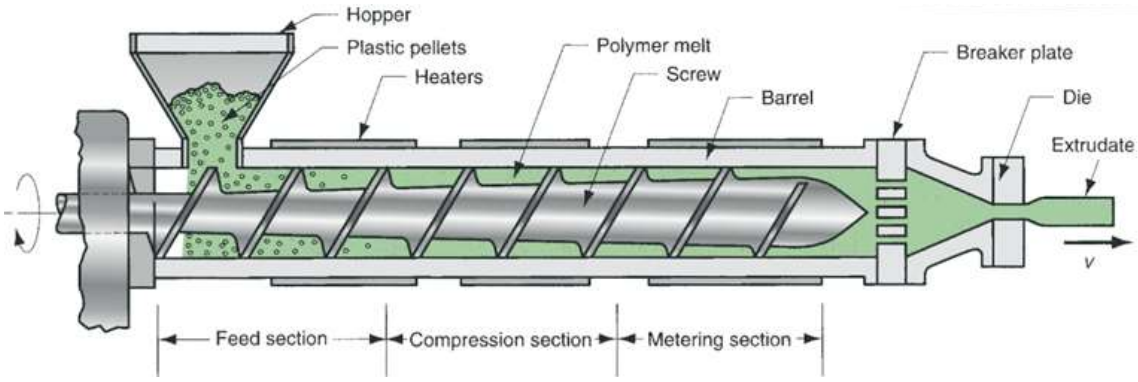

Figure 3. Schematic representation of single-screw extruder components and features for plastic and elastomer extrusion. Adapted from (Groover, 2012, p. 272).

4. DISCUSSION

None of the described techniques from Table 1, search for the existence or analyses concentrations of the toxic substances described in Section 2, which implies that the introduction of additional chemical analysis would be required if these toxic substances were to be discovered. If that were the case, it would radically increase the entry barrier for recyclers and further reduce already low degree of recycled plastic (Latinović & Jovanović, 2019). Finally, a legitimate question arises as to, what would then be the possibilities to exclude such materials from recycling, in a small-scale recycling plant e.g., when even large-scale recyclers struggle with different separation methods to increase the proportion of recycled plastic waste? There are always more questions than answers, and Brosché et al. (2021) took a significant step in the right direction with their proposals. Unfortunately, as it was shown, some of those substances represent constituents, rather than additives, such is Bisphenol A in the production of polycarbonates. After a large number of studies that showed the harmfulness of these additives, their “safe” substitutes appeared. However, even for new “safe” substitutes, there are now new emerging evidence of their harmfulness, too. So, we have got a circulus vicious in which certain toxic substances are being replaced by “novel safe substitutes”, which are later shown to be toxic as well, but all the while plastics are being hyperproduced. It would be reasonable to ask, do we have time to wait for eventual emergence of truly harmless products, or has that time already passed and radical moves ought to be played?

CONCLUSION

Based on the findings, we argue that the current state of the art in mechanical plastic recycling is inadequate in terms of environmental safety, which makes this specific part of the circular economy inapplicable at this time, thus further ranking non-creation of waste to the top primary goal. Governments should make radical cuts in the sense of a complete ban on the circulation of certain groups of products on the market, including the production, import, export and recycling of those products that contain the described, but also other toxic substances. One of the reasons for radical cuts is the possibility of control and punishment, because it does not require complex laboratory analyses and requires a smaller number of controlled places. We propose, in the first period and as soon as possible, a complete ban on the use of all single-use polymer packaging. This would inevitably lead to an increase in the prices of those products that relied on disposable packaging, a decrease in turnover, which would certainly have a negative economic effect. However, evidently, in the long term, this would have a significant positive impact on the environment and biota, while, on the other hand, it could be expected that, as always, the market will adapt to the new situation.

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