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A Survey on Detection of Plastic-Related Chemicals in Beer Packaged in PET Using FT-IR Technology

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Abstract: The emerging consciousness on nano- and microplastics in our environment raises questions on how to reduce and minimize its influence on human health. PET (polyethylene terephthalate) packaging is gaining popularity, and many traditional products end up in such packaging (vinegar, wine, beer). Currently, it is very hard to quantify the number of particles and their exact composition, but semi-quantitative techniques such as FT-IR (Fourier Transform Infrared Spectrophotometry) can give us an insight into the chemical composition of plastic bits in foods and beverages. Nowadays, beer is packed in PET packaging, since it provides a cheaper packaging material compared to glass and since it is safe to use at public manifestations, contrary to glass bottles, while providing a reasonable barrier for gas permeation (O_2 and CO_2). The aim of this paper was to provide a short overview of FT-IR-detected compounds in PET-packaged beer samples. The results indicate that many compounds can be found in beer, but those that were most commonly found in our research were β-cyclodextrin and L(-)-glyceraldehyde unnatural forms, two compounds designated as plastic-related compounds.

Keywords: plastics; FT-IR; beer; PET packaging; GC-MS

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1. Introduction

The existence of microplastics in the environment is known from the 1970s, but not until 2004 did this become more interesting for scholars [1–5]. Today, even the greater public is obtaining more and more worrying information about these harmful contaminants. Lately, much attention has been paid to discovering where and how microplastic gets into the environment and ends up in humans and animals. Although firstly recognized as an environmental contaminant, today more and more studies report microplastic particles and chemicals in foods and beverages. This is due to the ubiquitous application of plastic materials in the food and beverages industry and in packaging materials. EFSA (European Food Safety Agency) defined microplastics as, "For this statement, they are defined as a heterogeneous mixture of differently shaped materials referred to as fragments, fibers, spheroids, granules, pellets, flakes or beads, in the range of 0.1–5000 µm. A distinction can be made between primary and secondary microplastics. Primary microplastics are plastics that were originally manufactured to be that size while secondary microplastics originate from fragmentation of larger items, e.g., plastic debris" [6].

Beer is one of the beverages that can be packaged in PET (polyethylene terephthalate) packaging material. Even though PET bottles are very transport-friendly, weigh less than glass bottles, have good barrier properties against gas permeation, and are cheaper, they are often frowned upon when it comes to beer packaging. However, their proliferation in the world's beer market is more and more notable [7]. PET containers are breaking into the European market and even taking over traditional brewing countries (Czechia) that were adamantly against this idea just a few years ago. As a matter of fact, according to the

Pira International Ltd.'s report [8], in 2015, 5 billion PET bottles were present in the Central and Eastern European beer market, as opposed to Western Europe, where this number reached < one billion (799 million) bottles used for beer packaging annually. The biggest holdback to using PET bottles for beer involves the consumer's preference for glass or a can [8].

Until recently, the most important shortcoming of PET bottles was gas permeability, where CO_2 diffuses from the package and oxygen is prone to infuse the bottle, lessening the quality of beer in a short time (changes occur after 3–4 months) [7]. However, recent studies suggest that microplastic material (chemicals, micro-, and nanosized particles) could cause more problems than simple gas permeability. Namely, microplastic is designated as a hazardous material, and current studies aim to estimate how and where microplastics can be found. Further research involves the possibilities of the reduction and minimalization of such particles and chemicals in the environment. Additionally, harmful consequences to humans and animals are yet to be determined [9–12].

Since Croatia displays a significant consumption of beer and many of the beers can be found packaged in PET bottles, the aim of this research was to conduct a screening of possible microplastic material that can be found in commercially available beers packaged in PET bottles.

2. Materials and Methods

2.1. Sample Preparation and Analysis

For this research, various brands of beers packaged in 2 L PET packaging were purchased at the local supermarket. Sixteen different PET-packaged beers were bought and subjected to sample preparation and analysis. All beers were bought at the same day, from the same supermarket.

Samples were firstly subjected to filtration through a 70-mm-diameter Whatman cellulose filter paper with a pore size of 11 µm, grade 1. To avoid any outside contamination, the glass funnels were rinsed with acetone, as well as the laboratory beakers in which the sample was collected. Laboratory personnel handled all samples wearing cotton lab coats and sterling nitrile powder free exam gloves throughout the experimental procedure. After the filtration, filter papers were placed into clean and acetone-rinsed Petri dishes using a sterilized and acetone-rinsed pincette. Petri dishes were immediately closed upon placing the filter paper. One clean, unused filter paper was set as a background control for FT-IR. It too was placed into the Petri dish following the above-described procedure. All samples were filtered in duplicates.

Sample analysis on an attenuated total reflectance (ATR) FT-IR instrument (Spectrum Two, PerkinElmer, Waltham, MA, USA) was conducted by placing the background paper (control filter paper) on an FT-IRATR light source after it was cleaned with methanol using a paper towel. A diamond prism was used as the ATR accessory. All further samples followed the same procedure, and after each sample, the instrument was cleaned with methanol. Samples were placed onto the instrument using a methanol-rinsed pincette, while wearing gloves. The methanol used was Sigma-Aldrich (Darmstadt, Germany) HPLC grade 99.9%, packed in 3 L brown glass bottles. Measurements were carried out in a ventilated room using a triple-HEPA filter recuperator, at a room temperature of 25 °C. To control for changes in atmospheric CO_2 and H_2O levels, the machine's Atmospheric Vapor Compensation feature was turned on. FT-IR reads were analyzed with the Perkin–Elmer (Waltham, MA, USA) Spectrum IR 10.7 software. All samples were analyzed in duplicate.

The reads were subjected to compound analysis compared to several Perkin–Elmer libraries. The libraries were the Perkin–Elmer Raman Polymer Library, Perkin–Elmer Raman Library of Controlled Substances, Perkin–Elmer POLYSTYRENE library and Perkin–Elmer Fluka library.

2.2. Statistical Analysis

Data analysis was carried out in Microsoft Excel. The mean scores of compounds were calculated along with incidence frequencies in both replicates of all 16 samples ($n = 32$). To calculate incidence frequencies, the top 10 scores from the Spectrum 10 software database were used. Following the methodology from the surveyed literature, differences between spectral responses between different samples were visually scored for differences.

3. Results and Discussion

We are surrounded with plastic materials. This is no longer a matter of plastic pollution in the environment but of microplastic materials and chemicals that are flooding our food and bodies. Since beer is a widely spread beverage, it can be found in all parts of the world. Beer can be packaged into different packages, such as cans, glass bottles, or PET bottles, as well as in bulk packages like kegs. PET packaging is currently considered as the weakest packaging material in terms of gas permeability. However, PET packaging can also result in beer being contaminated with different microplastic materials, and the results obtained in this research indicate that microplastics can indeed be detected in such beer samples.

Specifically, all of the samples of analyzed beers have been subjected to the same procedure, and as a result, all of them showed detectable levels of several microplastic chemicals. The list of detected chemicals can be seen in Table 1. PET production includes many chemicals and additives that ensure the appropriate packaging characteristics. Depending on the product, the characteristics and chemicals are combined to provide the best packaging material. For example, for beer it is important to reduce the gas permeability as much as possible, so it is important to include relevant chemicals (i.e., 3-aminopropyltrimethoxysilane) in the packaging production.

Table 1. List of detected chemicals.

Chemical	Application	Number of Positive Samples
β-cyclodextrin	Encapsulation material, additives to plastic packaging films [13]	16
L(-)-glyceraldehyde unnatural form		16
Thiodiethylene glycol	Plasticizer [14]	6
α-cyclodextrin	Encapsulation material [13]	16
Tomatine	Surfactant, emulsifier [15]	16
3-(2-imidazolin-1-yl)propyltriethoxysilane	Additive for inorganic modification of block copolymers [16]	16
3-aminopropyltrimethoxysilane	Oxygen-barrier film in PET packaging [17]	16
Heptyl-β-d-glucopyranoside	Encapsulating material [18]	16
D(+)-glucose anhydrous	Brewing adjunct	16
Bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane		7
Dimethyl vinylphosphonate	Flame retardant [19]	7
Digitonin	Permeabilization of *Saccharomyces cerevisiae* cells [20]	2
Amygdalin		7

Not all chemicals detected in our research can be designated as microplastics, but the majority of them are related to packaging material. Most of them are used as additives to PET plastics.

Even though there are recent studies that investigate microplastics in foods and beverages [20–27], not many references describe the exact microplastics-related chemicals in certain foods, which rendered this research rather pioneering. However, there are some studies focusing on microplastics pollution in the oceans' flora and fauna that mention certain chemicals that are also detected in this research [28]. Based on this crucial paper, the authors could compare the obtained results and confirm that the found chemical could be designated as a microplastic. The analysis of different beers packaged in PET packaging resulted in several main datasets: all samples contained β-cyclodextrin and L(-)-glyceraldehyde unnatural forms with an average search score of over 60%. According to [28], these chemicals can be related to microplastics, since the research that Caron et al. conducted analyzed microplastic fragments, and the best hit for several samples was the L(-)-glyceraldehyde unnatural form. The microplastic material that was analyzed was in all cases designated as a transparent particle/film. Even though they hesitated to relate this chemical to microplastics, they suggested that this was probably part of plastic material. Namely, recent advances in polymer research resulted in glyceraldehyde being a substitute for the toxic formaldehyde originally used in the development of casein-based biodegradable plastics. It displayed equal characteristics in terms of the strength, stiffness, and compressibility of expanded polystyrene. However, a third of the material 'disappeared' within weeks [29]. Therefore, it is highly probable that these particles are indeed constituents of microplastics. Glyceraldehyde is a sugar, is water-soluble, and would dissolve in beer, which is obviously not the case in our research, meaning that this chemical had to be a stiffer compound, a kind of polymer, in order not to be dissolved in beer.

β-cyclodextrin, a compound also found in all samples, can be used in different industries such as tissue engineering, packing material, drug delivery, cosmetics, personal care and toiletry, waste management, catalysis adhesives, and coating [30].

Similarly, α-cyclodextrin was also found in PET-packaged beer but in just one sample. Thiodiethylene glycol is a known plasticizer [14] and can evidently be translated to beer via PET packaging. The toxicity of some of these compounds is yet to be determined, but they can certainly be found in many places. EFSA is currently considering the occurrence of nano- and microplastics in foods and beverages [31,32], and some chemicals have already been put under legislative limits (bisphenol A, polycyclic aromatic hydrocarbons). However, these efforts mostly relate to the physical appearance of nano- and microplastic materials, and there is no mention of various chemicals that get ingested into the system via detected nano- and microparticles. The results of this research point to the fact that many known-to-be-harmful and potentially harmful chemicals can be found in beer packaged in PET bottles and that this should be taken into account when considering the detrimental effect of nano- and microplastic materials found in humans and animals.

In Figure 1, accompanying Table 2, the frequency of incidence of each compound can be seen. Although compounds such as α-cyclodextrin, tomatine, 3-(2-imidazolin-1-yl) propyltriethoxysilane, 3-aminopropyltrimethoxysilane, and heptyl-β-d-glucopyranoside did not cross the 0.60 score threshold, the frequencies of their incidence in >90% of the assessed samples are indicative. 3-(2-imidazolin-1-yl) propyltriethoxysilane has several uses, but it is mainly used as a catalyst for condensation reactions, an additive for the inorganic modification of block copolymers, and a modifier for organically modified layered silicates [6]. According to [33], industrial silanes are commonly used as adhesives, sealants, coatings, and composites; 3-(2-imidazolin-1-yl) propyltriethoxysilane can be used as a coupling agent for elevated-temperature-cure epoxies. 3-aminopropyltrimethoxysilane is industrially used in plastic material and resin manufacturing and in plastic product manufacturing [34]. Heptyl-β-d-glucopyranoside is commonly used as an encapsulating agent [18] and can be attributed to PET material.

Table 2. Search scores above 60% for analyzed samples.

Sample Production Country	Prevalent Chemicals	Search Score
1. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
2. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
3. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
4. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
5. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
6. Czechia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
7. Czechia	β-cyclodextrin L(-)-glyceraldehyde unnatural form thiodiethylene glycol	
8. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form α-cyclodextrin thiodiethylene glycol	
9. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	>60%
10. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
11. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form thiodiethylene glycol	
12. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
13. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form	
14. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form thiodiethylene glycol	
15. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form thiodiethylene glycol	
16. Croatia	β-cyclodextrin L(-)-glyceraldehyde unnatural form thiodiethylene glycol	

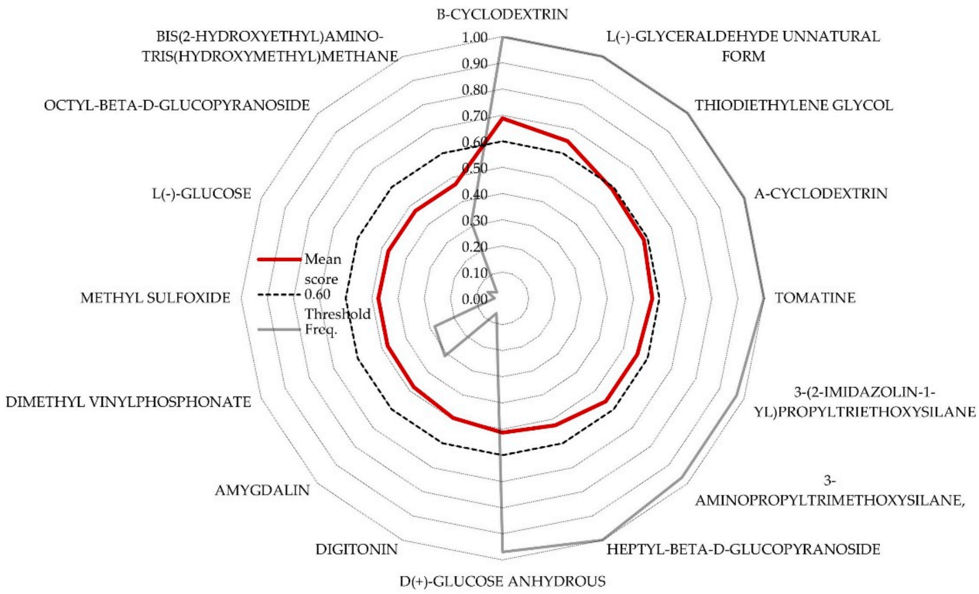

Figure 1. Radar plot with mean scores of the top 16 detected compounds in all samples, along with the 0.60 score threshold and frequency of appearance in top 10 hits from the compound database.

The compound thiodiethylene glycol appeared in 6 of 16 samples with an average score > 60%, and the transmittance of the sample with the detected compound (sample 16) was plotted against the transmittance of the sample in which the score of thiodiethylene glycol did not cross the 0.60 threshold (Figure 1). The visual resemblance of the transmittance patterns indicated the similar production/packing practices of both beer samples, with possibly different origins of raw materials causing the differences in transmittance at 500 to 900 and 3100 to 3400 cm^{-1} wavelengths (Figure 2).

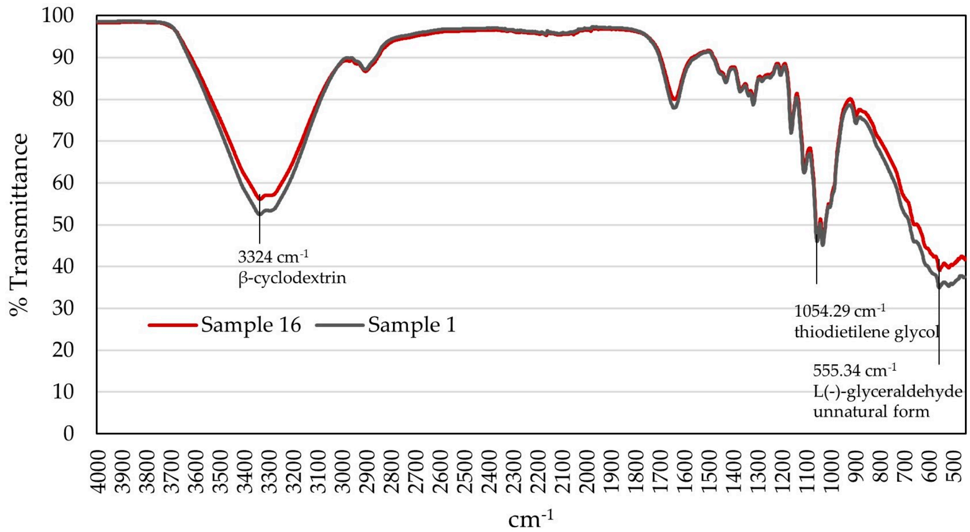

Figure 2. Transmittance reads of samples 16 (with detected thiodiethylene glycol) and 1 (without detected thiodiethylene glycol) at full FT-IR spectra from 450 to 4000 cm^{-1}.

Even though the found chemicals are not microplastic polymers, they can certainly be attributed to plastic materials such as additives, plasticizers, flame retardants or encapsulating materials, and therefore, they can be considered a part of microplastics. However, this was a screening of microplastic compounds that could be found in beer packaged in PET plastics, and further investigations should certainly include a visual examination.

All other compounds detected in this research (Table 1) were not included in the discussion, since the search score was below 60%. However, further studies should be conducted to establish their presence in beer packaged in PET packaging.

4. Conclusions

Most common microplastic chemicals detected in this research were β-cyclodextrin and L(-)-glyceraldehyde unnatural forms. There were many other detected chemicals in each sample, but the search score was under 60%, which was not sufficiently significant data. Even though this study revealed the presence of certain chemicals designated as microplastics in beer bottled in PET packaging, further investigations are planned in order to elucidate which microplastic-related chemicals can be found in beer and to investigate the influence of the type of packaging on the occurrence of chemicals. However, since there are no literature data about the exact chemicals in microplastics and since most papers describe the nano- and microplastic particles found under a microscope, it is important to deepen studies and broaden them to include the harmful potential of chemicals that can be reduced, replaced with some less harmful substances, or even expelled from PET or PEN (polyethylene naphthalate) plastic production that is used in many aspects of human life. Reducing plastic materials and chemicals in food and beverage containers will not solve the general problem of microplastics, since animals and the environment (plants, earth) absorb microplastics that litter ecosystems. On that note, this calls for radical change in general polymer-packaging-materials production, but we can certainly make a start by focusing on food and beverage containers.

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