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Physical and chemical characterization of representative samples of recycled rubber from end-of-life tires

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HIGHLIGHTS

- A large number of ELTs were sampled and classified by type, age and origin.
- Selected recycled tyre rubber samples were characterized.
- PAH contents were homogeneous and fell within in a narrow range.
- Recent ELT recycled rubber had a reduction H-bay index than older material.
- PAH characterization can be employed to calculate the H-bay index.

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ABSTRACT

A large number of end-of-life tires (ELTs) were sampled and classified by type, age and origin to obtain recycled rubber samples representative of the materials placed on the Italian market. The selected recycled tire rubber samples were physically and chemically characterized and a chemometric approach was used to determine correlations. The polycyclic aromatic hydrocarbons (PAHs) content was correlated to the aromaticity index and a model was built to establish the H-Bay aromaticity index (H-Bay) from the PAH concentrations. ELT of different origin and age produced in non-European countries generally had higher PAH content and a higher H-Bay index. H-Bay values of all the samples were lower than the REACH limits and old tires had higher aromatic content than recent ones, possibly due to the replacement of aromatic oils in tire production.

1. Introduction

Every year in Europe about three million tons of tires reach the end of their life (so-called end-of-life Tires, ELTs) and are sent for recovery/recycling at dedicated facilities (www.etrma.org). The radical changes in end uses of recycled tire rubber have raised several points regarding environmental and human safety, especially for people spending time in the facilities where recycled rubber has been employed. Many attempts have been made to evaluate the toxicity of recycled materials used for artificial turfs and playgrounds. Traces of hazardous chemicals, such as polycyclic aromatic hydrocarbons (PAHs) and heavy metals, have been analyzed together with their bio-accessibility, in order to develop safer strategies and solutions (Marsili et al., 2014; Selbes et al., 2015; Zhang et al., 2008). A recent study on pavers and playground materials concluded that the use of recycled tire rubber should be restricted because of the high concentration of toxic chemicals: many PAHs reached high levels in the samples analyzed and in the vapor phase available for inhalation (Llompart et al., 2013). However, other studies defined the risk level from recycled tire rubber as acceptable for human health and for the environment (Birkholz et al., 2003; ChemRisk, 2013; Ginsberg et al., 2011;

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Kanematsu et al., 2009; Moretto, 2007; Pavilonis et al., 2014) and some researchers did not find significant differences between artificial turf field/playground air and urban areas (Lim and Walker, 2009; Schilirò et al., 2013). Results from a study published by the Environmental and Occupational Health Sciences Institute of New Jersey show concentrations of metals (beryllium, magnesium, titanium, vanadium, chromium, copper, arsenic, selenium, silver, cadmium, mercury and lead), PAHs and semi-volatile compounds in infill and turf products for use on athletic fields and public parks at "low concentrations", with minimal exposure and risk for users. No risk assessment was recommended, considering the very low levels of metals and organic compounds found in bio-fluids (Lioy et al., 2011).

Despite the variety of previous studies, some common weaknesses should be highlighted: the analyses were carried out mainly on limited numbers of samples; the ELT origin of the materials analyzed was generally taken for granted, with no certain validation (Bocca et al., 2009; Dye et al., 2006) the types of recycled tires (truck and bus, T&B or passenger car tires, PCT) and their average ages were mainly unknown, with few exceptions (Lim and Walker, 2009; Nilsson et al., 2005; Sadiktsis et al., 2012). In 2010, REACH introduced a new regulation (entry no. 50 of Annex XVII, Regulation (EC) 1907/2008) which prohibited the use of aromatic oils in the production of tires, replacing them with new oils with lower PAH content. REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) is a European Union regulation, which entered into force on 1 June 2007, adopted to improve the protection of human health and the environment from the risks of chemicals. Most of the existing studies referred to experiments on infill samples without any age classification, so it is possible that ELTs in these studies were placed on the market before REACH restriction.

The aim of this study was to characterize recycled tire rubber based on the sampling plan of a significant number of ELTs, following standard procedures (ISO 2859-1, which specifies sampling plans and test procedures for attributes of discrete product units), in order to depict a more indicative sample of the Italian situation based on production year, manufacturing site and tire type.

2. Materials and methods

2.1. Sampling and production of rubber granules and powders

The method and the sizes of the samples were established according to ISO 2859-1 "Sampling procedures for inspection by attributes" (ISO 2859-1, 1999), and the sampling of granulated materials according to CEN/TS 14243: 2010. The study was run in five facilities in different Italian regions between October 2014 and January 2015. Sampling at each facility was done in several steps, described below.

1) Accumulation: a quantity of ELTs corresponding to 2–3 days of recycling facility collection (not less than 50 tons) was accumulated and "mixed" with a claw crane to make the mixture as homogeneous as possible. Small PCT tires were kept separate from medium T&B ones.
2) Reduction of the ELT samples: a representative sample of ELTs was obtained by dividing and mixing the piles using a claw crane and the ELT samples were stored separately from other deposits. An average of 13,000 kg of ELTs were sampled per facility.
3) Separation in batches/classification: the accumulated tires were then classified by trained technicians and separated into homogeneous batches identifying them by date of production and place of production.
4) Granulation: the four sub-batches of ELTs were granulated separately, avoiding any contamination by materials processed previously. The crumb materials were granules with nominal particle size 0.8–2.5 mm/2–4 mm and powders with nominal particle size 0–0.8 mm.
5) Sampling the granules and powders of known origin: during the granulation of the ELTs, at least 25 increments of 400 g of each size were collected to produce a primary sample. The use of a riffle splitter, as from CEN TS 14243:2010 (Materials Produced From End Of Life Tyres - Specification Of Categories Based On Their Dimension(S) And Impurities And Methods For Determining Their Dimension(S) And Impurities) gave a representative sample from the sub-batch.
6) Characterization and storage of the samples: the primary samples were further reduced to have smaller representative samples for characterization. These samples were delivered to the different laboratories for physical and chemical characterization.

The certification agency Bureau Veritas was oversaw all the sampling and classification phases and the sealing of all the samples and the big bags of recycled rubber sent for characterization and use. All the phases of preparation, shipping and receipt of the samples were conducted according to the *chain of custody* principle.

2.2. Characterization of rubber granules and powders

2.2.1. Physical characterization

Physical analyses were done according to CEN/TS 14243: 2010.

Particle size distribution was analyzed using an Endecotts Octagon Digital vibro sifter with 200 mm diameter sieves of mesh dimension suitable for each sample according to the technical requirements and testing standard (ISO 3310-1, 2016).

Free metal content was determined as the amount of free steel separated by an Alga N35 magnet before the sieving procedure. Free textile content was determined by manual separation of the compacted textile balls formed after the sieving. Other impurities of crumb rubber consist of the amount of soil powder and other external contaminants. These were determined after the previous analyses by decanting the resulting material in a water solution of $CaCl_2$ using a separatory funnel. The impurities were weighed after filtration, washing with water and drying.

2.2.2. Leaching of heavy metals

The content of metals leached into water was determined according to DIN 18035-7: 2002-06 for lead, cadmium, total chrome, hexavalent chrome, mercury, zinc and tin. About 100 g of material were extracted twice for 24 h in a bottle with 1000 mL of CO_2 -injected deionized water. The bottle was shaken during the extraction to remove gas bubbles. Zinc was determined in deionized water. About 100 g of sample were added to 1000 mL of deionized water and shaken for 24 h at room temperature. The sample was filtered and treated a second time with fresh water. The heavy metals concentration was quantitatively determined on the second extracts using a Thermo Fisher M6 AA System AAS acetylene (or nitrous oxide) flame atomic absorption and graphite furnace spectrophotometer.

2.2.3. Zinc content

For the zinc content, 10 mL of nitric acid were added to a rubber crumb sample (about 0.2 g) and transferred to a Milestone-FKV Ethos 1 microwave oven. The solutions were concentrated to a final volume of 50 mL. Zinc concentration was measured with the