



# 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 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.

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## 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](http://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 (Lompart 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; Sadiqsis 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<sub>2</sub> 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<sub>2</sub>-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

atomic absorption spectrophotometer and expressed as the mean of three replicates as the percentage of ZnO.

#### 2.2.4. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were done with a Mettler Toledo TGA/SDTA851e according to ISO 9924-1 (ISO 9924-1, 2016). ISO 9924-1 consists of a number of standard procedures to determine the composition of vulcanizates and uncured compounds presented in rubber and rubber products by thermogravimetry. About 10 mg of crumb rubber samples were placed in an alumina crucible. The content of volatile matter at 300 °C was determined under a 60 mL/min nitrogen flow, heating the samples and following the specific temperature from 70 to 300 °C at 10 °C/min then keeping the temperature constant at 300 °C for 10 min. The polymer content was determined under a nitrogen flow by heating the samples from 300 to 550 °C at a rate of 20 °C/min and keeping the temperature constant at 550 °C for 15 min. Carbon dioxide release due to calcium carbonate degradation was identified in the same condition by heating from 550 to 900 °C then keeping the temperature constant for 10 min. For carbon black, the stream was switched from nitrogen to air with a flow rate of 60 mL/min and the temperature was kept at 900 °C until constant weight. The ash content was evaluated as the residue at the end of analysis.

#### 2.2.5. Aromaticity index ( $H_{\text{Bay}}$ )

The aromatic character of the oils in the crumb rubber samples was assessed by the  $H_{\text{Bay}}$  method according to ISO 21461, (ISO 21461, 2012) (Pan et al., 2016). The sample was extracted for 8 h with acetone and the extract was evaporated to dryness under a stream of nitrogen. After weighing the extract, a suitable amount of n-heptane necessary to bring the concentration to 100 mg/mL was added and three 1-mL vials were prepared. The solution from one vial was transferred onto the Solid Phase Extraction (SPE) cartridge (SampliQ Silica, 500 mg, Agilent Technologies, Waldbronn, Germany). The non-polar fraction was eluted with 25 mL of n-heptane, maintaining a constant solvent flow (5 cm<sup>3</sup>/min). The eluted residue was evaporated to dryness under nitrogen and the dry residue was weighed to calculate the recovery percentage. The procedure was repeated with the other two vials and the result was presented as the average of the three recovery percentages. The hydrogen atoms in the bay region, characteristic of aromatic oils were identified by <sup>1</sup>H NMR spectroscopy and the percentage of bay region hydrogens (%  $H_{\text{Bay}}$ ) was calculated according to the standard for the three purified extracts. The spectra were recorded on a Bruker 300 Ultrashield NMR (Bruker, Massachusetts, U.S.A.) spectrometer and CDCl<sub>3</sub> was used as solvent to dissolve dry residue.

#### 2.2.6. Polycyclic aromatic hydrocarbons

Each individual sample has been analyzed in duplicate and PAHs were determined by gas chromatography–mass spectrometry (GC–MS) analysis. About 1 g of tire powder or granules were added to 80 µL of a solution of 10 ng/µL deuterated PAH-Mix9 (Dr. Ehrenstorfer GmbH, Augsburg, Germany) and 25 mL of hexane:dichloromethane (1:1). The solution was extracted for 30 min using an ultrasound bath at 80 °C and 8 mL of sample were filtered on a VWR glass microfiber filter and concentrated to about 0.5 mL under nitrogen. Clean-up was done with a Florisil Chromabond column (1000 mg/6 mL, particle size 150–250 µm, Macherey-Nagel, Germany) with dichloromethane and hexane. After evaporation of the solvent under nitrogen, 200 µL of acetone and 8 mL of ultrapure water were added to the sample. Solid phase micro extraction was done with a 7 µm PDMS fiber (Sigma-Aldrich, Missouri, U.S.A.) immersed in the aqueous phase at 80 °C for 30 min. GC analysis was carried out on an Agilent 7890 GC gas chromatograph equipped with an Agilent 5975 mass spectrometer (Agilent Technologies,

Waldbronn, Germany). The transfer line was set at 280 °C, the quadrupole at 150 °C and the ion source at 230 °C. PAHs were separated with a J&W Scientific DB-5MS (length 30 m, I.D. 0.25 mm, film 0.25 µm) with helium as carrier gas (constant column flow 1.0 mL/min). The GC oven temperature program was set from 50 °C (held 2 min) to 200 °C (held 1 min) at a heating rate of 10 °C/min and then to 300 °C at 5 °C/min (held for 8 min). Splitless mode was used for injection. After 30 s, the split was opened at a flow of 50 mL/min and the injector temperature was kept at 270 °C. The mass spectrometer operated in the sim/scan mode with the mass range of 40–700 *m/z*. Analysis time was 25 min and a nominal value of the electron multiplier was set 200 V higher than the auto-tune. The selected ion monitoring (SIM) method was used as acquisition mode (benzo[*a*]anthracene: RT 27.54, *m/z* 228; benzo[*a*]anthracene-D12: RT 27.44, *m/z* 240; chrysene: RT 27.68, *m/z* 228; chrysene-D12: RT 27.57, *m/z* 240; benzo [*b+j*]fluoranthene: RT 32, *m/z* 252; benzo[*b*]fluoranthene-D12: RT 31.9, *m/z* 264; benzo[*k*]fluoranthene: RT 32.11, *m/z* 252; benzo[*k*]fluoranthene-D12: RT 32.04, *m/z* 264; benzo[*e*]pyrene: RT 33.02, *m/z* 252; benzo[*a*]pyrene: RT 33.21, *m/z* 252; benzo[*a*]pyrene-D12: RT 33.13, *m/z* 264; dibenzo[*a,h*]anthracene: RT 37.42, *m/z* 278; dibenzo[*a,h*]anthracene-D14: RT 37.31, *m/z* 292). The 15 PAHs determined by this method are reported in Table 1. Since no ELT reference material was available, the method was validated with NIST Standard Reference Material, using certified urban dust particulate material, showing an average recovery of 98 ± 7.5% (mean ± SD) of the certified PAHs values in the reference material.

### 3. Results and discussion

#### 3.1. Sampling

The sampling plan implemented at five ELT recycling facilities was aimed at characterizing in detail the type, age and country of production of the tires collected and recycled as rubber granules and powders. In total, 3885 ELTs, corresponding to over 63,800 kg were classified and a database with the information and pictures of all these tires was created. Over 70% of ELTs were manufactured by European factories; among the non-European tires, about 20% were of Far East origin (most from China, Japan and Korea), 4% from Turkey and the remaining 4% were produced in other countries (like America and Africa). Classification by age showed that less than 15% were more than seven years old, with about 20–25 years for the oldest. The percentage of rubber from T&B tires varied between 8 and 100%. The rubber samples had variable T&B/PCT ratios and can be considered representative of the materials usually produced by ELT reuse.

A specific classification of the collected ELTs was done in the light of the restriction entry no. 50, Annex XVII of Reg. (EC) 1908/2008 enforced in 2010 for all tires placed on the European market. Four main classes were identified taking into account their European or non-European origin (EU/no-EU) and if they were produced before or after 2010 (ANTE/POST). At each facility after classification, the different types of tires were granulated separately and characterized. Further a sample was taken from the production as commercial reference for each facility (Unsorted) in order to represent the composition of the rubber from mixed ELT that is usually placed on the market.

Most samples were characterized by nominal particle size of granules (0.8–2.5 mm), commonly used to infill artificial turf football fields. Only samples from facility 1 had a lower nominal size (0.2–0.8 mm), because they produce only powder from T&B tires (Table 1).

**Table 1**  
Classification and characterization data of granulated recycled tire rubber samples.

Sample ID	Recycler	Age	Origin	T&B <sup>a</sup> (%)	Nominal size (mm)	Surface Area <sup>b</sup> (m <sup>2</sup> /g)	ML 300 <sup>c</sup> (%)	Polymer (%)	CO <sub>2</sub> (%)	CB <sup>d</sup> (%)	Ash (%)	Acetone Extract (%)	Recovery (%)	H-Bay (% range)	Sum 8 PAHs (mg/kg)	Sum 15 PAHs (mg/kg)
1	1	ANTE	EU	100	0.2–0.8	9.03E-03	6.69	58.99	3.213	27.05	4.05	5.3	40.47 ± 1.1	0.25 (0.24–0.26)	4.78	40.40
2	1	ANTE	No-EU	100	0.2–0.8	7.82E-03	6.76	57.70	1.909	26.34	7.27	5.8	45.03 ± 1.84	0.24 (0.23–0.25)	5.82	52.95
3	1	POST	EU	100	0.2–0.8	1.06E-02	5.77	58.17	2.486	26.61	6.95	5.1	37.3 ± 1.31	0.11 (0.10–0.12)	4.32	45.06
4	1	POST	No-EU	100	0.2–0.8	1.03E-02	10.73	51.05	2.697	26.30	9.17	5.2	39.77 ± 1.07	0.13 (0.13–0.13)	5.05	50.62
5	1	Unsorted	–	100	0.2–0.8	1.02E-02	6.75	57.87	2.427	26.20	6.75	5.6	36.27 ± 1.5	0.22 (0.21–0.22)	5.78	44.68
6	2	ANTE	EU	100	0.8–2.5	3.25E-03	5.95	60.41	0.686	28.26	4.71	4.7	55.03 ± 0.49	0.20 (0.19–0.21)	4.10	36.90
7	2	ANTE	No-EU	100	0.8–2.5	3.18E-03	6.59	57.45	0.687	29.38	5.88	5.6	46.7 ± 1.01	0.33 (0.31–0.36)	9.86	47.49
8	2	POST	EU	100	0.8–2.5	3.34E-03	6.70	59.24	0.569	29.59	3.88	5.1	44.83 ± 1.2	0.09 (0.09–0.10)	3.85	38.60
9	2	POST	No-EU	100	0.8–2.5	3.07E-03	6.41	60.71	0.000	29.15	3.58	5.1	42.6 ± 1.56	0.09 (0.09–0.10)	4.16	44.50
10	2	Unsorted	–	100	0.8–2.5	3.31E-03	6.38	57.59	0.000	30.36	5.66	4.9	49.97 ± 1.33	0.19 (0.18–0.19)	6.91	51.94
11	3	ANTE	EU	76	0.8–2.5	3.42E-03	7.09	57.01	0.000	30.24	5.65	6.1	56.13 ± 0.86	0.27 (0.25–0.29)	5.83	42.97
12	3	ANTE	No-EU	68	0.8–2.5	3.37E-03	7.61	59.14	0.000	29.92	3.31	8.7	60.1 ± 0.98	0.25 (0.24–0.26)	8.21	52.69
13	3	POST	EU	64	0.8–2.5	3.37E-03	7.06	56.48	1.007	25.68	9.77	6.7	55.33 ± 1.59	0.15 (0.14–0.15)	3.78	38.46
14	3	POST	No-EU	56	0.8–2.5	3.28E-03	6.65	55.56	0.606	32.94	4.23	7.6	56.87 ± 0.49	0.15 (0.15–0.16)	4.98	43.30
15	3	Unsorted	–	65	0.8–2.5	3.14E-03	7.73	60.97	0.000	23.64	7.65	9.2	60.7 ± 0.87	0.21 (0.19–0.22)	6.90	50.79
16	4	ANTE	EU	72	0.8–2.5	2.73E-03	9.03	54.33	1.374	29.21	6.03	8.0	60.57 ± 0.32	0.21 (0.20–0.21)	5.38	44.50
17	4	ANTE	No-EU	41	0.8–2.5	2.60E-03	7.77	55.04	0.541	12.20	24.46	9.1	57.83 ± 0.9	0.21 (0.19–0.22)	7.15	49.05
18	4	POST	EU	61	0.8–2.5	2.81E-03	7.34	59.56	0.000	28.75	4.35	6.9	54.9 ± 2.43	0.18 (0.17–0.19)	5.50	41.74
19	4	POST	No-EU	33	0.8–2.5	2.86E-03	7.40	58.05	0.758	29.80	3.98	7.5	60.4 ± 0.3	0.28 (0.28–0.29)	11.76	59.82
20	4	Unsorted	–	58	0.8–2.5	2.82E-03	8.95	54.85	0.739	28.51	6.98	8.3	60.8 ± 0.92	0.20 (0.18–0.23)	7.10	53.73
21	5	ANTE	EU	38	0.8–2.5	3.75E-03	7.10	52.49	0.000	30.22	10.16	12.1	57.67 ± 0.35	0.19 (0.18–0.20)	4.97	42.56
22	5	ANTE	No-EU	62	0.8–2.5	3.53E-03	8.08	56.09	0.000	29.78	6.02	9.2	64.13 ± 0.46	0.21 (0.18–0.22)	10.42	65.39
23	5	POST	EU	13	0.8–2.5	3.59E-03	8.13	57.81	3.250	23.76	7.03	9.3	61.97 ± 0.55	0.20 (0.18–0.20)	6.47	49.50
24	5	POST	No-EU	8	0.8–2.5	3.44E-03	9.62	56.17	0.000	23.21	10.97	9.1	61.67 ± 0.32	0.22 (0.21–0.24)	9.09	52.61
25	5	Unsorted	–	23	0.8–2.5	4.06E-03	7.30	58.31	0.000	29.96	4.43	8.6	58.5 ± 0.26	0.22 (0.22–0.23)	9.99	56.46

<sup>a</sup> Percentage of Truck and Bus tires.

<sup>b</sup> Calculated from the experimental particle size distribution taking into account the max sieve diameter for each size range.

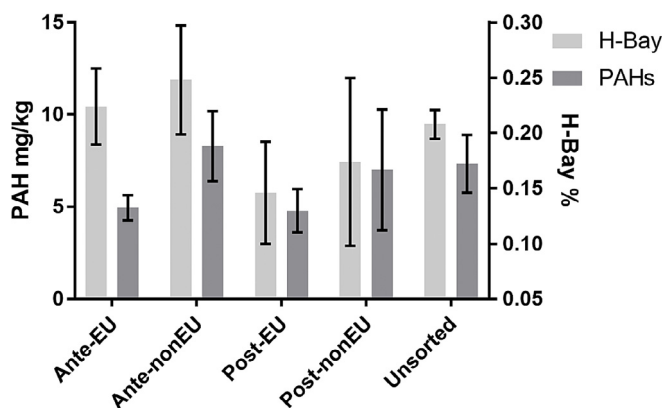
<sup>c</sup> Mass Loss at 300 °C.

<sup>d</sup> Percentage of carbon black.

### 3.2. Physical and chemical analysis of granulated recycled tire rubber samples

The physical properties, zinc content and the leaching of metals are reported as averages of the 25 samples classified and analyzed. The values for free metal, free textile and other impurities were respectively <0.01%, 0.11 ± 0.06% and 0.29 ± 0.03% (mean ± SD). There was an acceptable degree of cleanliness of the recycled rubber produced by all the facilities. Zinc is the metal most investigated in published studies on account of its substantial amounts, its high leaching capability (Li et al., 2010) and its toxic properties for some organisms, especially in aquatic environments (Jelmert and van Leeuwen, 2000). The analytical result for Zn leaching

was 0.10–3.00 mg/L (min–max), in line with the last few years for zinc content in tire rubber where in single samples values ranged from 0.002 to 62 mg/L, while average Zn in rubber was 1.82% (1.06–2.38%, min–max) while previous data reported contents average values of 1.02% (0.01–1.94%, min–max) (Bocca et al., 2009; Menichini et al., 2011). However, the zinc concentration cannot be considered the only parameter for evaluating of its effect on the environment (Kruger et al., 2013). Leachable metals provide a valid reference for environmental effects. The values measured (0.0050 ± 0.0007 mg/L for Pb; 0.6040 ± 1.36 mg/L for Zn (mean ± SD); Cd, Cr VI, Hg and Sn undetectable) are on average very low, often below the detection limit. TGA can give a picture of the chemical composition of rubber materials. The results are very



**Fig. 1.** Comparison of the H-Bay index and the sum of eight priority PAH contents. Significant differences between Ante-EU vs. Post-EU ( $p$  value < 0.05) for H-Bay index and Ante-EU vs. Ante-nonEU ( $p$  value < 0.01) for PAH contents were observed (unpaired  $t$ -test).

similar for all 25 samples (Table 1). No particular differences are seen with respect to age and origin of the samples and the average composition (7.49% Mass loss at 300 °C, 57.24% Polymer, 28.17% Carbon black and 6.14% Ash at 900 °C) is almost the same as the basic composition of tire rubber.

The H-Bay aromaticity index identifies plasticizing oils used in the production of the tires. REACH entry 50 requires the H-Bay index not to exceed 0.35%; the H-Bay results for all 25 samples (Table 1) are below this limit. The classified data (Fig. 1) indicates that old tires have higher aromatic content than more recent ones. This shows that most of the ELTs recycled today are compliant with REACH and that tire manufacturers began to replace aromatic oils before 2010, to guarantee compliance of the tires sold from that year.

PAH analysis from NIST reference material showed that the method gave an average recovery of 96.9% for priority PAHs, with an average RSD of 3.6% on triplicate analysis.

Fig. 1 also reports the averages for the eight priority PAH contents for the five classifications of ELTs. These indicate a generally lower amount of PAHs in EU recycled rubber samples than in no-EU

ones and the same held true for H-Bay. Moreover, for the no-EU material there was a distinguishable difference for the PAH contents between the ANTE and POST classes, while this was less evident for the EU ones. The Unsorted samples had almost the same average PAH and H-Bay values as the classified samples.

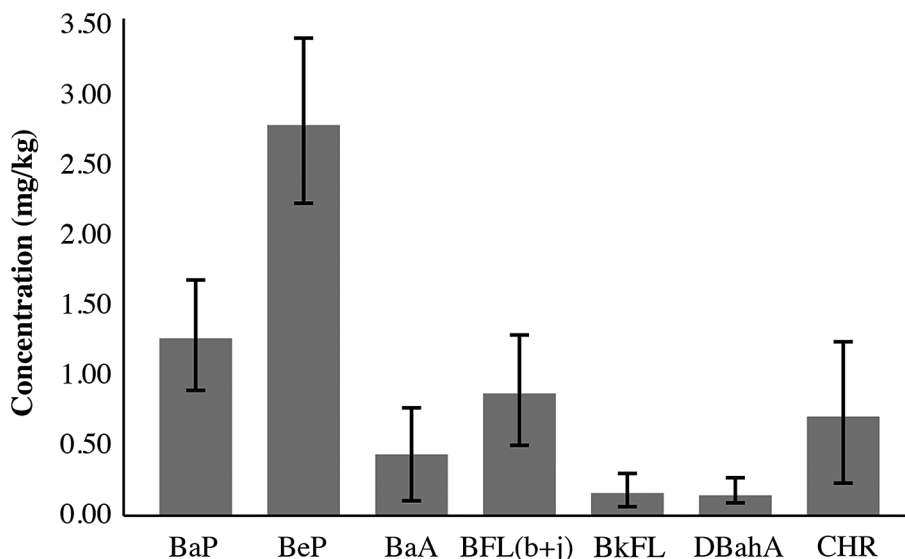
The REACH restriction states that extender oils can be used in tires only if the oils contain less than 1 mg/kg (0.0001% by weight) benzo[*a*]pyrene (B[*a*]P) and 10 mg/kg (0.001% by weight) of the sum of 8 priority PAHs (Bergmann et al., 2011). This means that in tire rubber the sum of the eight priority PAHs from oils should not exceed 1 ppm and the remainder should be due to carbon black. “Fingerprint” of the eight priority PAHs for the recycled tire rubber were defined based on the experimental results (Fig. 2). Comparison with data published by various authors (Llompart et al., 2013; Marsili et al., 2014; Menichini et al., 2011; Ruffino et al., 2013) shows the variability of the PAH concentrations reported. For example, the data given by Ruffino et al. are higher than those presented here, with benzo(*a*)anthracene as much as ten times greater. Llompart et al. (2013) too reported PAH content generally higher than those found in present samples, and are not in agreement with the results given by other authors. One possible explanation could be the different types of rubber (gaskets, conveyor belt materials, etc.) in the commercial materials used for artificial turfs or playgrounds (Dye et al., 2006).

### 3.3. Chemometric analysis

A Principal Component Analysis (PCA) of the data in Table 1 and all the PAH concentrations was carried out to identify the main correlations among the recycled tire rubber properties. The loading plot of principal components (PC) 1 vs. 2 is reported in Fig. 3a.

From the loadings plot on PC1 we see mainly information about the PAHs concentrations and the value of H-Bay, which form a large cluster on the left to negative values of PC1. Consequently, in the score plot, all scores with negative PC1 values have high PAHs and H-Bay values, while scores with positive values of PC1 (like all EU clusters) have low PAHs and H-Bay values.

On PC2, however, the information about the TGA’s macroscopic composition is mainly seen. Specifically, scores with negative values indicate high values of ash, ML300 and CO<sub>2</sub>, while scores



**Fig. 2.** PAH fingerprints in rubber recycled from all ELTs samples. Legend: Benzo[*a*]pyrene (BaP), Benzo[*e*]pyrene (BeP), Benzo[*a*]anthracene (BaA), Benzo[*k*]fluoranthene (BkFL), Benzo[*b*+*j*] (BFL(b+j)), Dibenzo[*a,h*]anthracene (DBahA), Chrysene (CHR).

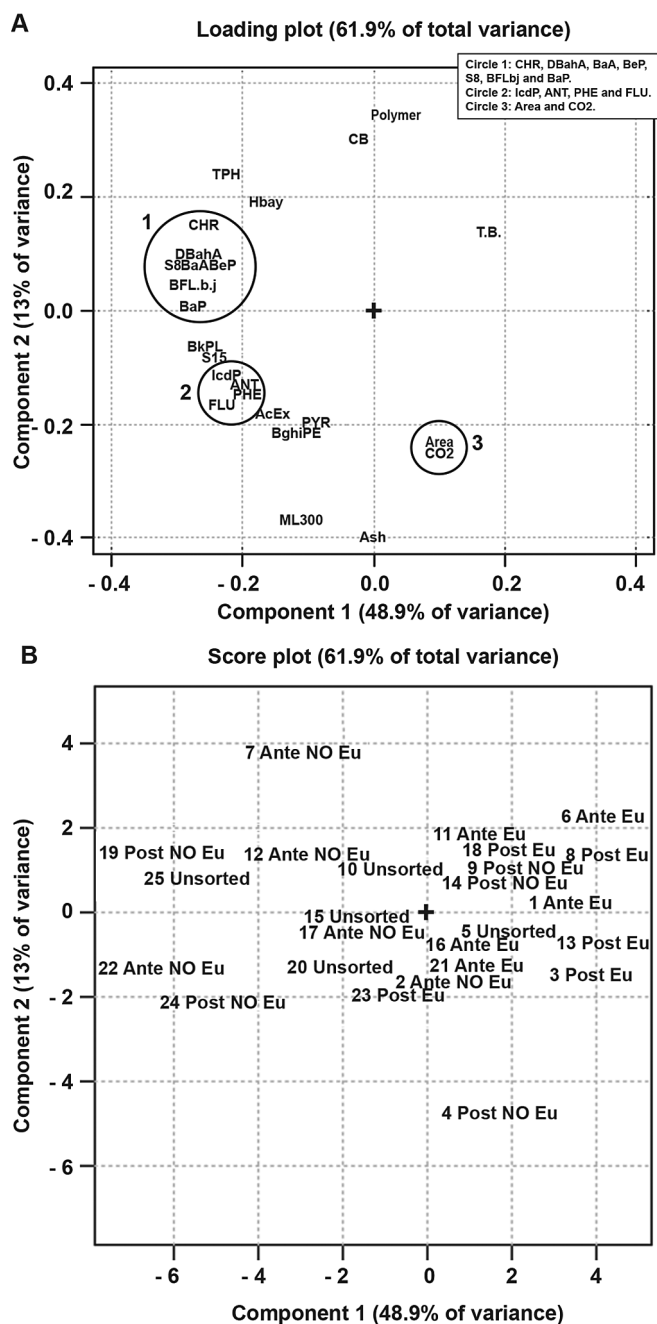


Fig. 3. Loading plot (A) and score plot (B) PC1 vs. PC2 of the variables and samples in Table 1 with the concentrations of the 15 PAHs (Table 2).

with positive values of PC2 indicate high concentrations of Polymer and Carbon black values. Also the H-Bay value brings a positive contribution to PC2, although less evident than that expressed in PC1. Among the main correlations, acetone extract (AcEx) and mass loss at 300 °C (ML300) are on the same side of the plot, opposite T&B, possibly pointing to an inverse correlation due to the lower content of oils in T&B tire rubber than PCT. The surface area (Area) and CO<sub>2</sub> almost overlap. This close link depends on the fact that the first five samples in Table 1 are powders and not granules, and for this production the recycler uses calcium carbonate as anticaking agent.

All the PAH concentrations, the sums of eight priority (S8) and all fifteen (S15) can be found on the left in plot together with the H-

Table 2

Coefficients of the model for the evaluation of H-Bay using the PAH concentrations as variables.

Compound	Symbol	Model coefficient
Benzo[a]pyrene;	BaP	0.015042418
Benzo[e]pyrene	BeP	0.016008768
Benzo[a]anthracene	BaA	0.022993877
Benzo[fluoranthene(b+j)	BFL(b+j)	0.020111815
Benzo[k]fluoranthene	BkFL	0.005834606
Dibenzo[a,h]anthracene	DBahA	0.107554228
Chrysene	CHR	0.018249843
Phenanthrene	PHE	-0.01414994
Anthracene	ANT	-0.020421861
Fluoranthene	FLU	-0.008992961
Pyrene	PYR	-0.004259325
Triphenylene	TPH	0.031218756
Indeno[1,2,3-cd]pyrene	IcdP	0.005681797
Benzo[g,h,i]fluoranthene	BghiPE	-0.004436962
Constant	-	0.198671802

Bay. All 15 analyzed PAHs can be seen in Table 2. The positions of these variables highlight their strong correlations and are deeply discriminating factors in the analysis of the samples especially on PC1. Moreover, some of the PAHs, specifically total petroleum hydrocarbons (TPH), chrysene (CHR), dibenzo[a,h]anthracene (DBahA), benzo[a]anthracene (BaA), benzo[e]pyrene (BeP), Benzo[fluoranthene [b+j] (BFLbj) and benzo[a]pyrene (BaP), are closer to H-Bay than the others and so apparently more closely correlated. A summary examination of the chemical structures of these compounds indicates that they have among the most influence in H-Bay due to the presence of bay and pseudo-bay regions (Harvey and Dunne, 1978).

The strong discriminating effect of PAHs and H-Bay means that the sample's ages and origin in relation to their composition can be examined. Fig. 3b reports the score plot of the 25 samples, with the ANTE vs. POST and European (Eu) vs. non-European (No-Eu) distinctions. The reference samples, Unsorted, are also indicated and are almost all in the middle of the graph, confirming that these samples have average properties. The Eu samples are quite close, forming a cluster on the right side of the plot, indicating that they have small amounts of PAHs and low H-Bay. Instead, the No-Eu samples are dispersed over the whole plot. These considerations reflect the time of classification ANTE/POST: almost all the European tire producers began to replace plasticizer oils before 2010, while there is no particular evidence for the No-Eu ones.

The correlation between the PAH contents and the H-Bay confirmed by PCA led us to build a model for estimating H-Bay using the PAH concentrations. This is very useful considering that NMR is not as widespread among the research institutes and control authorities as PAH determination.

Partial Least Squares regression (PLS1) was done and a model was created, arbitrarily using data from four recyclers as training set (samples 1–20) and the fifth recycler data as evaluation set (samples 21–25). There were five cross validation segments and two used components. The characteristics of the model were a Root Mean Square Error (RMSE) in Cross Validation of 0.04670, and a RMSE in Prediction of 0.03266 with a BIAS in Prediction of -0.009686. Table 2 reports the model coefficients for each PAH variable. The similarity of RMSE in prediction and validation indicates that the method is adequate for calculating the H-Bay of a sample by PAH analysis.

#### 4. Conclusions

A large sample of ELTs in five different facilities was collected in Italy, according to ISO standards, and individually sorted by origin,

age and type. Four classes were identified in the light of the REACH restriction of 2010, depending on their origin (Europe or not) and their age (before and after 2010). In each facility, the tires were processed separately in order to produce different samples of rubber of known origin and age. The samples were also compared with recycled tire rubber taken from production, as commercial references. The sampling procedures followed, and the sample size means the 25 samples studied can be considered representative of Italian production of recycled tire rubber between 2014 and 2015.

The samples were chemically characterized and the results statistically analyzed. Thermogravimetric analysis indicated that the average composition of the samples was consistent with the basic composition of commercial tire rubber, with only negligible differences among the samples. The H-Bay aromaticity index for all the samples were lower than the standard limit and the results showed that old tires had a higher aromatic content than recent ones, possibly due to the replacement of aromatic oils in production. PAH determination showed the data were homogeneous and fell within a narrow range. Average PAHs values of all ELT samples were within REACH restrictions for extender oils as the sum of 8 priority PAHs (<10 mg/kg), but not as BaP content (<1 mg/kg). PAH content was significantly lower in European recycled tires than non-European ones, while other differences were not statistically significant. There was a strong correlation between H-Bay and PAH analysis and the model for H-Bay evaluation from PAH content gave an indicative value without directly doing the analysis.

The chemical characterization of these representative samples in the Italian market showed that concentrations in controlled origin materials (European samples) were lower than in uncontrolled samples (non European samples), highlighting the importance of accurate material selection to guarantee acceptable levels of residual contamination.

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