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CHARACTERIZATION OF CRUMB RUBBER FROM END-OF-LIFE TYRES FOR PAVING APPLICATIONS

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SUMMARY: Crumb rubber (CR) derived from grinding of end-of-life tyres (ELTs) may be successfully used as a bitumen modifier or as a supplementary component in the production of bituminous mixtures employed for the construction and maintenance of road pavements. However, CRs deriving from different sources and processes yield effects on performance under traffic loading and on gaseous emissions produced during laying on site which may change considerably depending upon their physical and chemical properties. In order to quantitatively assess the possible variability of CR characteristics, samples were taken from 9 Italian and 2 foreign ELT processing plants. Investigation activities included field surveys, during which plants were examined in detail, and laboratory tests, which focused on physical and chemical characterization of CR. Based on the analysis of available technical information and experimental data, it was possible to find relationships between the peculiar characteristics of treatment cycles and corresponding CR properties.

KEY WORDS: crumb rubber, end-of -life tyres, paving applications, physical chemical characterization

1. INTRODUCTION

Management of end-of-life tyres (ELTs) has become a critical problem worldwide due to the increasing number of vehicles circulating in the road network and to the crucial role that mobility has assumed in society development. Since landfill disposal has been banned in most Countries, alternative final destinations have been sought, with a major effort being placed in trying to exploit in the most efficient manner the high energy potential of ELTs. Nevertheless, due to the fact that rubber employed in tyre fabrication is the result of specialized materials' selection, recycling and reuse seem to be preferable options for such a high-quality waste material (Santagata and Zanetti, 2012).

Practical experience and research have shown that crumb rubber (CR) derived from grinding of ELTs may be successfully used as a bitumen modifier or as a supplementary component in the production of bituminous mixtures employed for the construction and maintenance of road pavements. Available technologies can be grouped into two main categories which are associated to the so-called "wet" and "dry" production processes. Within each group, different versions of the technology have been conceived and subjected to trials either in the laboratory or at the industrial scale, in the constant attempt of exploiting more efficiently the performance-related benefits of CR.

In the "wet" process, CR is preliminarily mixed with bitumen, thus obtaining a ductile and elastic modified binder, known as "asphalt rubber" (ASTM D6114-09), that is then combined with aggregates in the hot mix plant. Resulting mixtures are generally of the gap-graded (GG) or open-graded (OG) type, characterized by a very high binder content (of the order of 7.5-10% b.w. of dry aggregates) and by a non-continuous particle size distribution that allows CR to be accommodated within the composite material. GG and OG mixtures are employed for the formation of surface courses and have earned a satisfactory reputation with respect to field performance (Hicks, 2002).

In the "dry" method, CR is introduced in the production flow of bituminous mixtures as a supplementary component, substituting part of the aggregates and providing enhanced elastic response under loading (Santagata and Zanetti, 2012; Santagata et al., 2013). Mixtures are usually of the dense-graded (DG) type, with a continuous particle size distribution and an optimal binder

53 content (usually of the order of 5-6%) which is only slightly higher than that adopted for standard
54 mixtures containing no recycled rubber (Buncher, 1995). Unfortunately, the performance record of
55 these mixtures has been quite inconsistent, with the frequent occurrence of early ravelling
56 phenomena and moisture-related damage (Amirkhanian, 2001; Caltrans, 2005). This also explains
57 the limited diffusion of such a technology, with full-scale applications that have been generally
58 carried out locally rather than at the network level.
59 For both the abovementioned technologies, concerns have been raised on the use of CR in
60 bituminous mixtures with respect to its potential contribution to gaseous emissions during production
61 and laying, and to the possible consequences which it can cause on the health of construction
62 workers. However, a limited number of experimental studies have been carried out on this specific
63 topic, with no clear quantification of the actual hazardous effects of CR (Watts et al., 1998; Burr et
64 al., 2001; Stout and Carlson, 2003).
65 The Authors have recently contributed to this area of technical knowledge by applying to pavement
66 works risk analysis concepts developed in previous studies focused on the evaluation and
67 remediation of contaminated sites (Marescalco and Zanetti, 2010; Zanetti et al., 2013b) and on the
68 approval of the use of CR in artificial turf sports fields (Ruffino et al., 2013). In particular, by
69 considering the results of analyses carried out on gaseous emissions sampled on site or in the
70 laboratory in controlled conditions, comparisons have been made between bituminous mixtures
71 containing CR (produced by employing both the “wet” and “dry” technology) and bituminous
72 mixtures of the standard type (Zanetti et al., 2013a, 2014a and 2014b).
73 Based on the Authors’ experience, it can be concluded that CRs deriving from different sources and
74 processes yield effects on field performance and emissions of bituminous binders and mixtures
75 which may change considerably depending upon their physical and chemical properties. In turn,
76 these are dictated by the characteristics of ELTs subjected to processing and by the phenomena
77 which occur during the various phases of ELT treatment (shredding, magnetic separation,
78 granulation, milling and sieving).

In order to quantitatively assess the possible variability of CRs, in the study described in this paper, samples were taken from 9 Italian and 2 foreign ELT processing plants and thereafter subjected to laboratory investigations for the assessment of physical and chemical characteristics. In particular, experimental tests were carried out for the determination of particle size distribution, density, cleanliness, particle shape and morphology, specific surface area, content of metals, PAHs (polynuclear aromatic hydrocarbons) and VOCs (volatile organic compounds) and elemental analysis. Based on the analysis of technical information and experimental data, it was possible to find relationships between the peculiar characteristics of treatment cycles and corresponding CR properties.

2. BACKGROUND

2.1 CR production

Processing of ELTs is carried out in various phases during which rubber is separated from other materials (textile fibers and metals), mechanically reduced in granular form and finally divided into particle size fractions. When shredding, shear and abrasion operations occur with no specific temperature conditioning, the process is known as “ambient size reduction”. In some plants, however, ELTs are brought below rubber glass transition temperature with adequate cooling systems and the resulting process is referred to as “cryogenic”. Moreover, novel processing methods are continuously developed in order to optimize plant efficiency. As an example, size reduction has also been attempted by means of the “high pressure waterjet” system, based on the abrasive effects caused by water jets at 3.000 bar which pulverize ELTs.

Depending upon the type of treatment process and on the origin of ELTs fed to it, CR may have different physical and chemical characteristics. In particular, particles deriving from ambient size reduction generally have irregular shape and rough surface; moreover, it has been postulated that in some cases heat generated during mechanical processing may induce a partial devulcanization of rubber. By comparison, cryogenically produced CRs are mostly made of cuboid-shaped particles

with a smooth surface. With respect to ELT origin, it is well known that tyre producers employ different rubber formulations and that truck tyres generally have a higher natural rubber content than car tyres. However, in practice only the second factor may influence CR production since there are plants that treat only truck (or car) tyres, but none are dedicated to a single tyre producer.

2.2 CR-bitumen interaction

In the asphalt rubber "wet" production process, CR is thoroughly mixed with bitumen at a temperature in the 175-225°C range. The resulting binder is then kept in agitation at high temperature (150-215°C) for the time period (of the order of 45-60 minutes) which is necessary for interaction phenomena between the components to occur. In particular, CR particles are partially digested in the bituminous matrix and absorb part of the aromatic fraction of bitumen, with a resulting volume expansion and formation of a gel-like surface coating which gives the binder its peculiar physical and rheological characteristics (Way et al., 2012). In this form, CR particles are still visible in the composite binder which has a distinctive granular-like appearance. If curing is carried out at an excessive temperature and/or for a too long time period, degradation phenomena become prevalent and CR is totally digested in bitumen: as a consequence, the resulting binder does not have the typical characteristics of asphalt rubber and may exhibit unsatisfactory performance. Asphalt rubber binders usually have a CR content comprised between 18 and 22% (b.w. of total binder), with a high viscosity at storage/mixing temperatures and enhanced elastic properties in service. Binder characteristics are dependent not only upon chemical composition of employed components, but also on CR dosage, particle size and morphology. In such a context, it has been proven that the intensity of the above described interaction phenomena tends to increase with CR dosage and specific surface area (Shen et al., 2009). Therefore, CRs which are considered more reactive are those which are finer, constituted by rough, irregular particles.

In the production of "dry" mixtures CR is usually employed with a dosage comprised between 1% and 3% (b.w. of dry aggregates). Depending upon the type of plant, either batch or drum-mix, CR can be introduced in the production flow of bituminous mixtures by means of different methods, but

is always added to the heated aggregates before coming in contact with bitumen. When this condition occurs, even though CR particles are not digested in bitumen, they do absorb part of its aromatic fractions. However, such an interaction takes place in non-controlled conditions, starting from the mixing process in the plant and progressing throughout the early phases of service life (Santagata et al., 2013). Studies performed in the past have shown that in this respect beneficial effects can be obtained by pretreating CR by means of function-specific catalysts (Epps, 1994) or extender oils (Newcomb et al., 1994; Khalid and Artamendi, 2002).

2.3 CR selection and acceptance

Selection and acceptance of CR for use in asphalt rubber classically relies upon the requirements that have been set in ASTM D6114. These are expressed in terms of cleanliness (fiber content < 0.5%; metal content < 0.01%), moisture content (< 0.75%), density (equal to 1.15 ± 0.05) and maximum particle size (2.36 mm). However, the standard also specifies that the exact size distribution of CR should be agreed upon between producer and end-user.

Based on experience and local tradition, in other contexts requirements may be slightly different. As an example, technical specifications of the California State Department of Transportation require the use of natural and synthetic rubber in given proportions and provide size distribution acceptance intervals which should be satisfied by single CR components (Caltrans, 2003).

In the case of the “dry” production technology, depending upon the desired effect on the resulting bituminous mixture, CR can be employed with different size distributions, ranging from “ultrafine” (entirely passing the 0.3 mm sieve) to “coarse” (passing the 6 mm sieve and totally retained on the 2.36 mm sieve) (Caltrans, 2005). Since it has been recognized that size distribution (and related specific surface area) is the main factor controlling performance properties of “dry” mixtures, specific requirements are usually not set on other CR characteristics.

Physical and rheological properties of asphalt rubber are also subjected to acceptance requirements in technical specifications. This is done either by referring to the results of classical empirical tests (penetration, softening point, etc.) or by considering viscoelastic properties measured at

representative temperatures, frequencies and ageing conditions. All evaluation systems also include acceptance criteria referred to apparent viscosity, which is typically required to be comprised between 1500 and 5000 mPa·s. Such a property, which refers to the flow behavior of asphalt rubber, is considered as a good quality indicator that can be also measured on site, from storage tanks, with portable hand-held viscometers.

3. EXPERIMENTAL INVESTIGATION

The investigation described in this paper was carried out by considering 16 CRs sampled from 9 Italian and 2 foreign plants. Experimental activities included field surveys, during which processing plants were examined in detail, and laboratory investigations, which focused on CR physical and chemical characterization. Tests were carried out in the "Road Materials Laboratory" (RML) and in the "Environmental Chemistry Laboratory" (ECL) of the Politecnico di Torino

3.1 Plant surveys

Treatment processes of the plants which were considered in this study are synthetically described in Table 1. The majority of them (9 out of 11) operate by mechanical size reduction at ambient temperature, one is of the cryogenic type (G) and one relies upon the waterjet technology (H). With respect to ambient size reduction processes, it can be observed that the number and type of consecutive working phases changes considerably, thus affecting the characteristics of final products. In general terms, more recent plants (e.g. B and E) tend to have multiple iron magnetic separation phases in order to ensure a greater purity of CRs; moreover, multiple shredding/milling phases may be combined with the purpose of increasing production flexibility (i.e. of widening the range of possible CR products).

Table 1. Description of ELT processing plants.

Phases	ELT processing plants										
	A	B	C	D	E	F	G	H	I	J	K
Primary shredding	×	×	×	×	×	×	×*	×**	n.a.	×	×
Iron magnetic separation					×				n.a.	×	
Secondary shredding		×			×	×	×*		n.a.		×
Cold granulation		×	×						n.a.	×	
Iron magnetic separation	×	×	×	×	×	×	×		n.a.		×
Primary milling	×	×	×	×	×	×	×*		n.a.	×	
Secondary milling	×								n.a.		
Sieving	×	×	×	×	×	×	×	×	n.a.	×	×

(*) Carried out in cryogenic conditions
(**) Carried out with waterjet treatment.
n.a. Information not available.

3.2 CR chemical characterization

Chemical characterization of CR consisted in the determination of the contents of metals, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and elemental analysis (carbon, hydrogen, nitrogen and sulfur). Since there are no fixed standards which define procedures for CR characterization, tests were carried out by following protocols which were developed for such a purpose in the ECL. In all cases, duplicate measurements were performed for each test.

Metals were determined by using an inductively coupled plasma optical emission spectrometer (ICP-OES). Test samples were obtained by subjecting 0.1 g of CR to treatment in a microwave digestion unit in the presence of 1 ml perchloric acid (70%, Merck) and 3 ml of nitric acid (65%, Riedel de Haen, Sigma Aldrich). After digestion, samples were filtered (Whatman filters, 2.7 micron retention grade) and then transferred to 100 ml flasks where they were brought to full volume by means of distilled water. In ICP-OES analyses, elements which were detected through their electromagnetic radiation after excitation included those which derive from residues of the metal structure of tyres and those which are present due to contamination.

198 Determination of VOCs and PAHs was carried out by means of solvent extraction and
199 gas-chromatographic analysis. A 2 g CR sample was extracted with 20 ml of CH_2Cl_2 kept for 20
200 minutes in a microwave oven set at 600 W. Analyses were then performed by using an Agilent
201 7890/5975 gas chromatograph equipped with a HP5-MS capillary column (30m×0.25mm×0.25μm)
202 and combined with a mass spectrometer detector (GC-MS). VOC and PAH compounds were
203 considered in the investigation since they are potentially toxic or carcinogenic substances.
204 Carbon, hydrogen, nitrogen and sulphur contents were determined by employing a Flash 2000
205 ThermoFisher Scientific CHNS analyzer which operates according to the dynamic flash combustion
206 technique on 2-3 mg CR samples. After combustion of the sample, reaction gas products were
207 carried by helium flow to a copper-filled layer, then through a GC column that provided separation
208 of the combustion gases and finally detected by a Thermal Conductivity Detector.

209 **3.3 CR physical characterization**

210 Physical characterization of CR was carried out by means of laboratory tests for the determination of
211 particle size distribution, density, cleanliness, particle morphology and specific surface area.
212 Particle size distribution was evaluated in dry conditions by making use of sieves of the Tyler series
213 (ASTM E-11, 2000). Since electrostatic effects may make this type of analysis quite difficult,
214 especially in the presence of high percentages of very fine material, intense mechanical agitation of
215 the sieve column was required. At least three repetitions were considered necessary in order to have
216 representative results. Data was also cross-checked with those derived from image analysis,
217 described further on in the context of morphology evaluation.
218 Density (ρ) at 25°C was measured with the pycnometer method (EN1097-7, 2008) by employing
219 ethylic alcohol as fluid of known density in order to prevent particles from floating to the surface.
220 Relative density (i.e. specific gravity, SG) was thereafter calculated by referring measured density to
221 that of water at the same temperature.

Evaluation of the degree of cleanliness (presence of textile fibers, metal residues and other contaminants) was performed in qualitative terms by means of observations with a stereomicroscope. For such a purpose, images were acquired with a digital camera and thereafter visually examined. Use of stereomicroscope observations was also the starting point of the technique used for the assessment of morphological characteristics and for the estimate of surface area (Santagata et al., 2012). However, in this case the plan-view digital image of the set of considered particles was processed with a freeware software (ImageJ, version 1.45, National Institutes of Health) which allows the identification and geometrical description of each particle.

The following morphological parameters were directly calculated from image analysis results:

- average value of the shape coefficient (C_f), given by the ratio between the maximum and minimum Feret diameters (maxF and minF) of each particle;
- average value of the solidity coefficient (C_s), given by the ratio between the area of each particle ($A_{particle}$) and the minimum convex area (A_{convex}) in which it is enclosed.

Surface area per unit mass (SA_m) was calculated by making use of the following expression:

$$SA_m = \phi \cdot \frac{6}{\rho} \cdot \sum_i \frac{f_i}{d_{m,i}} \qquad (1)$$

where: SA_m = surface area per unit mass (in m^2/g);

ϕ = corrective factor which takes into account morphology of constituent particles;

ρ = density (in g/m^3);

f_i = frequency (in decimal units) of the i-th size fraction;

$d_{m,i}$ = mean particle diameter (in m) of the i-th size fraction.

Corrective factor ϕ was derived from image analysis results by making use of analytical models which allow calculation of surface area per unit volume (SA_v) by referring to sets of ideal particles with different shape and roughness characteristics (Santagata et al., 2012). In particular, ϕ was

obtained as the product of two distinct corrective factors, ϕ_f and ϕ_r, which separately take into account the effects of shape and roughness, respectively.

4. RESULTS AND DISCUSSION

Results recorded during laboratory tests are synthesized in Tables 2-7 and in Figures 1-7. In general terms, as expected, it was found that sampled CRs represent a very broad spectrum of products for paving applications which may constitute a valuable reference database for future use. As discussed in the following, data analysis was carried out by highlighting relevant differences between products and by searching for relationships between investigated characteristics.

By taking into account measured size distribution, as required by the EN standard currently under development (CEN/TS 14243, 2010), CR samples were associated to alphanumeric codes given by the label of the production plant (from A to K) and the interval comprised between D_{10} and D_{90} (sieve openings corresponding to 10% and 90% passing, respectively). Thus, it was found that considered CRs can be grouped into three categories: "coarse" ($D_{90} > 1.0$), "standard" ($0.5 \leq D_{90} \leq 1.0$) and "fine" ($D_{90} < 0.5$). In such a context it should be mentioned that CR H 0-0.7, derived from waterjet production, although technically allocated to the "standard" category, has very peculiar characteristics as a consequence of its very broad size distribution which combines the presence of coarse particles (with size up to 2 mm) with a very high content of fines (14.3% passing the 0.063 sieve).

Particle size distribution curves are displayed in Figures 1a and 1b, while Table 2 lists the values of descriptive size distribution parameters which include D_{10} and D_{90}, D_{50} (which provides a measure of the overall coarseness/fineness), D_{80}/D_{20} (a uniformity factor which quantifies overall width of size distribution) and $P_{0.063}$ (percent passing the 0.063 sieve, corresponding to the content of the very fine particles).

It can be observed that among the "standard" CRs, considered as typical candidates for use in the production of asphalt rubber ("wet" process), the main factor which allows them to be discriminated

is $P_{0.063}$, which in fact is especially high in the case of the waterjet (H 0-0.7) and cryogenic (G 0.2-0.6) products. This observation proves that within a given category of CRs, significant differences in terms of size distribution can generally stem only from variations of production type. Similar observations apply to the category of "fine" CRs, usually employed for special applications as a result of their higher market value. It can be observed that plant B, which in comparison to the others (A and C) has a greater number of shredding/granulation/milling phases, yields the product with the highest percentage of very fine particles ($P_{0.063}$ equal to 59.9%).

No specific comments can be made on the "coarse" CRs due to the similarity of the two considered products and plants.

Figure 1a. Particle size distribution of the CR samples (plants A-E).

Figure 1b. Particle size distribution of the CR samples (plants F-K).

Basic physical characterization of CRs was completed by performing laboratory tests for the evaluation of density ρ (and specific gravity, SG). Corresponding results, listed in Table 2, are comprised within a narrow variation range (ρ = 1.158-1.223 g/cm^3; SG = 1.160-1.225), and show that most of the CRs of the "standard" category meet requirements set by ASTM (SG = 1.15 ± 0.05) for products to be used for the production of asphalt rubber. The most relevant deviation is exhibited by cryogenic CR G 0.2-0.6, which has a very high density value (1.223 g/cm^3), probably as a result of the peculiar morphological properties of its particles (cuboid-shaped and very smooth).

Since CR-bitumen interaction and properties of the resulting binder/matrix are strongly dependent upon particle morphology and specific surface area, these characteristics were assessed by means of adequate models applied to image analysis results derived from microscope observations. Examples of post-processing images of two CRs are shown in Figure 2, while results of the consequent analytical evaluation are given in Tables 3a and 3b and in Figures 3 and 4.

295 Morphological coefficients C_s and C_f were calculated from the geometry of the projection of CR
296 particles on the horizontal plane. While C_f refers to the degree of elongation, C_s reveals the presence
297 of surface irregularities which are responsible for a significant increase of total perimeter (and thus,
298 in the three-dimensional situation, of surface area).
299 It was observed that low C_f values, typical or regularly-shaped particles which are those desired for
300 the preparation of homogeneous blends/mixtures, may be accompanied, depending upon the specific
301 features of each CR (and of the originating production process), by either high or low values of C_s.
302 This is clearly shown in the shape-roughness mapping plot of Figure 3, built by representing C_s as a
303 function of C_f. Most of the considered CRs fall within the cuboid-rough (low C_f, low C_s; 5 CRs out
304 of 16) or in the cuboid-smooth quadrants (low C_f, higher C_s; 6 CRs out of 16). On the contrary, only
305 few of the analysed products are found in the elongated-rough (high C_f, low C_s; 3 out of 16) and
306 elongated-smooth (high C_f, higher C_s; 2 out of 16) quadrants.
307 It can be noticed that, as expected (Figure 2), cryogenic product G 0.2-0.6 is characterized by the
308 highest value of C_s, typical of smooth particles obtained from the low-temperature and high-impact
309 production procedure which causes brittle fracture of rubber granules. Results obtained for the CR
310 derived from the waterjet process (H 0-0.7) are also coherent with physical expectations, with a
311 similar shape (C_f of the order of 1.65) but a rougher surface caused by the abrasive action of high-
312 pressure jets.

313 Figure 2. Examples of post-processing images of two CR samples.

314 Figure 3. Shape-roughness mapping plot of CR samples.

315 Figure 4. Effect of CR coarseness/fineness on surface area per unit mass.

316 Variability of C_f-C_s results obtained for ambient size CRs is a consequence of the specific features of
317 the different production processes. However, it can be observed that the coarser products, even

318 though regular in shape, tend to have a smoother surface (C_s > 0.85). On the contrary, finer CR
319 products exhibit a rougher surface and the lowest C_s values are in fact associated to the lowest values
320 of parameter D_{50} (I 0.2-0.7, A 0.1-0.3, C 0.1-0.4, K 0.1-0.5 and B 0.1-0.4, all with D_{50} < 0.50 mm).
321 The above described variability of particle size distribution and morphological characteristics has an
322 effect on the specific surface area (per unit mass) of analyzed CRs, which is reported in Tables 3a
323 and 3b.
324 As expected, the highest and lowest surface area values are respectively associated to the "fine" and
325 "coarse" products (with average values equal to 0.0243 m^2/g and 0.0046 m^2/g), while "standard"
326 CRs exhibit intermediate SA_m values (mean equal to 0.0127 m^2/g). Such particle size dependency is
327 visually represented in Figure 4, where surface area is plotted as a function of the diameter
328 corresponding to 50% passing (D_{50}).
329 Results obtained from chemical analyses highlighted several common factors for all CRs, while
330 singularities were related to specific aspects of production, such as treatment (number and type of
331 ELT processing phases) and feed (type and conditions of ELTs, presence of non-ELT rubber).
332 Elemental analysis showed, as expected, that percentages of carbon and hydrogen are similar for all
333 CRs, with the exception of "coarse" ones (I 0.6-1.5 and J 0.9-2.2). Such a result is coherent with
334 density (and specific gravity) data, listed in Table 2, which exhibit a similar uniformity, with the
335 exception of cryogenic product G 0.2-0.6, and do not reveal an explicit dependency from the specific
336 features of production processes.
337 Nitrogen and sulphur contents, lower in absolute value, were found to be slightly more variable. The
338 latter element, used for rubber vulcanization, may be an indicator of the possible use of different
339 percentages of car vs. truck ELTs, of the selection of ELTs in specific conditions (depending upon
340 tread wear) and/or of the introduction in the processing plant of additional materials such as non-
341 vulcanized (raw) rubber and scrap rubber from other production processes.
342 Regardless of the elemental composition uniformity described above, CR samples were found to be
343 significantly different in terms of their level of cleanliness and purity, which was assessed by

344 evaluating content of metals by means of ICP-OES analyses. This can be appreciated by considering
345 the experimental data provided in Table 5 and in Figures 5a and 5b, where only the most relevant
346 elements have been displayed.
347 Whenever two different CRs were sampled from a same plant, metal content was found to be higher
348 in the finer fraction (i.e. products from plants A, B, C, I and J). This is due to the fact that as particle
349 size is reduced, separation of different components (rubber, steel, textiles) is more difficult.
350 Figure 5a. Metal content of CR samples.
351 Figure 5b. Metal content of CR samples.
352 By looking at the entire data set it can also be observed that the lowest metals' content is exhibited
353 by CRs J 0.9-2.2 ("coarse") and F 0.3-0.7 ("standard"), while the highest values were found in the
354 case of C 0.1-0.4 ("fine"). For such products overall ranking deriving from considering all major
355 elements was matched by the assessment focused on iron content, which ranged from 0.036-0.042%
356 (CRs J 0.9-2.2 and F 0.3-0.7) to 0.915% (CR C 0.1-0.4).
357 Singularities were detected for CRs produced by plants D and G, which were characterized by very
358 high values of lead (D 0.3-0.7) and calcium (G 0.2-0.6) content. Moreover, both products were found
359 to have out-of-range contents of barium. Anomalies of the barium content may be related to its
360 employment as a catalyst for the synthesis of polybutadiene rubber, while presence of excessive
361 calcium may derive from calcium hydroxide used for the anti-packing treatment of non-vulcanized
362 rubber which may have been introduced in the production flow of CR. Finally, probably as a result
363 of inefficient separation of residues coming from steel belts and bead wires, an exceptionally high
364 copper content was detected in CR C 0.1-0.4.
365 All products were found to have a zinc content greater than 1%, presumably due to the
366 corresponding oxide that is used as a vulcanisation aid in the rubber production process.
367 The significant variability of plant configuration in the case of ambient size reduction processes does
368 not allow a straightforward comparison between the three technologies in terms of cleanliness and

purity. However, results obtained for products G 0.2-0.6 and H 0-0.7 suggest that the cryogenic treatment may provide a better means for rubber-metal separation than waterjet blasting.

The observations provided above, based on analytical measurements, were supplemented by visual analyses of microscopic images which focused on the detection of foreign impurities (metals and textiles) not included in the rubber matrix. Examples of the assessment performed on the two CRs produced by plant C are given in Figure 6.

CR samples were subjected to laboratory tests for the determination of VOCs and PAHs since there are concerns whether the presence of recycled rubber in bituminous mixtures can affect the toxic and carcinogenic potential of gaseous emissions produced during laying on site. However, it should be pointed out that such an analysis was included in this study for comparative purposes only, since the Authors have already highlighted the fact that the dominating factors which control VOCs and PAHs released in the environment are bitumen type and quantity (Zanetti et al., 2013a and 2014a).

Results of VOC and PAH analyses are listed in Tables 6 and 7 and are synthetically represented, by referring to total contents, in Figure 7.

Figure 6. Examples of visual assessment of degree of cleanliness of two CR samples.

In the case of ambient size CRs, it can be postulated that results are dependent not only on plant feed (type and wear conditions of ELTs, possible presence of non-ELT rubber) but also on two additional factors which have a direct effect on the release of organic compounds in the environment during CR production. Both factors should be taken into account since they may cause a reduction of VOCs and PAHs which can be detected in the laboratory on the final product.

The first relevant factor is energy dissipation, which occurs, in the form of heat, during shredding and milling operations. Thus, as the number of such phases is increased, for example when passing from “coarse” to “standard” (or “fine”) products, lighter organic compounds in the CR are bound to be reduced. This is the case of products derived from plants I and J, which exhibit a total VOC content which decreases when considering finer products obtained by supplementary milling.

However, it is uncertain whether the same explanation can be given for VOC data obtained on

products coming from plants A, B and C, since the fine fractions may have been derived from the "standard" ones only by means of additional sieving (which causes no heating effects).

The second relevant factor is specific surface area. In fact, for a given production temperature, loss of VOCs is presumably more intense as specific surface increases and, as a consequence, CRs with a higher SA_m are expected to yield lower VOCs in laboratory analyses. As shown in Figure 8, such a physical expectation is matched by results found for CRs from plants A, B and C (and, to a more limited extent, from I and J) being the finer products those which possess a higher SA_m value.

Figure 7. VOC and PAH content of CR samples.

Figure 8. Effect of surface area on total VOC content of CR samples.

PAH contents do not show the same straightforward particle size and surface area dependencies of VOCs. This is coherent with the fact that such compounds, in the typical conditions which occur during ELT processing, are less prone to be released in the environment and are therefore mostly maintained within the rubber matrix of the final product.

Results obtained on CRs derived from cryogenic and waterjet production (G 0.2-0.6 and H 0-0.7) cannot be explained by referring to the same hypotheses outlined above since milling occurs in temperature conditions which are more tightly controlled. Thus, they should be considered mainly as a consequence of the characteristics of materials fed to production and do not allow any interpretation theory to be proposed.

5. CONCLUSIONS

Experimental data collected in the study described in this paper show that CRs for paving applications may have, depending upon their production process, physical and chemical properties which are comprised within very broad variation ranges. Such an observation is extremely relevant since significant variations may be reflected, as a consequence, in the bituminous materials in which CRs are included (either "wet" asphalt rubber binders or "dry" bituminous mixtures). Thus, several

key elements should be taken into account in the production of CRs and in their performance-oriented selection.

In order to maximize bitumen-CR interactions, which are of premium importance in asphalt rubber binders, evaluation of specific surface area should be included in CR standard characterization procedures. In fact, experimental data show that surface area depends upon particle size distribution, which can be controlled by adequately combining shredding, milling and sieving operations, and by particle morphology, which can be mapped by referring to image analysis parameters.

Cleanliness of CR products also plays a critical role in the performance of final binders and mixtures since textile and metal residues may impair homogeneity and act as damage initiators. In such a context, combined analysis of the metals' content and results of microscopic observations may be of support in identifying specific foreign elements and oxides and in implementing improvement measures in the processing of ELTs.

Chemical characterization of CRs with respect to organic compounds such as VOCs and PAHs is also of special interest as a result of their possible effects on gaseous emissions produced by composite bituminous binders and mixtures during laying operations. Although it has been already proven that emissions are more strongly affected by bitumen type and content and that the potential release of CR is in fact shielded by bitumen itself, analyses performed on CR may be of value at least in comparative terms. As highlighted in this paper, a reduction of such a potential may be obtained by selecting products derived from a greater number of shredding/milling phases and/or characterized by a higher specific surface area.

Further investigations are currently being performed in order to widen the existing CR database and to highlight in more detail relationships between CR characteristics and production features. A CR certification process is also under development with the purpose of providing the paving sector with an efficient tool for the selection of materials, processes and products.

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Table 2. Size distribution parameters, density and specific gravity of the CR samples.

	A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
Diameter with 10% passing (D_{10}) [mm]	0.42	0.11	0.30	0.15	0.38	0.09	0.27	0.27	0.27	0.24	0	0.57	0.17	0.94	0.25	0.13
Diameter with 90% passing (D_{90}) [mm]	0.69	0.33	0.68	0.38	0.69	0.39	0.70	0.55	0.67	0.56	0.74	1.50	0.69	2.21	0.56	0.54
Diameter with 50% passing (D_{50}) [mm]	0.54	0.23	0.51	0.27	0.54	0.23	0.51	0.45	0.50	0.42	0.28	1.04	0.41	1.48	0.35	0.29
Uniformity coefficient D_{80}/D_{20}	1.41	1.86	1.65	1.83	1.44	2.50	1.60	1.58	1.62	1.80	8.03	1.89	2.48	1.78	1.82	2.60
Percentage passing 0.063 mm ($P_{0.063}$) [%]	0.07	6.47	0.58	59.9	0.33	34.8	0.97	0.61	0.13	21.0	14.3	0	0.75	0	0	2.31
Density (ρ) [g/cm^3]	1.172	1.213	1.181	1.192	1.158	1.196	1.203	1.178	1.185	1.223	1.189	1.204	1.199	1.207	1.190	1.208
Specific gravity (SG)	1.174	1.215	1.183	1.194	1.160	1.200	1.206	1.181	1.188	1.225	1.192	1.207	1.201	1.210	1.193	1.210

Table 3a. Morphological parameters and surface area of the CR samples (plants A to E).

	A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6
Shape coefficient (C_f)	1.79	1.77	1.85	1.69	1.69	1.78	1.67	1.52
Solidity coefficient (C_s)	0.848	0.812	0.851	0.834	0.855	0.805	0.846	0.871
Shape corrective factor (ϕ_f)	0.955	0.973	0.918	0.924	0.978	0.930	0.833	0.894
Roughness factor (ϕ_r)	1.240	1.313	1.216	1.206	1.254	1.244	1.078	1.091
Corrective factor (ϕ)	1.184	1.277	1.117	1.115	1.226	1.157	0.897	0.975
Surface area per unit mass (SA_m) [m^2/g]	0.0112	0.0270	0.0111	0.0208	0.0118	0.0252	0.0088	0.0110

Table 3b. Morphological parameters and surface area of the CR samples (plants F to L).

	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
Shape coefficient (C_f)	1.63	1.63	1.66	1.65	1.74	1.54	1.76	1.63
Solidity coefficient (C_s)	0.879	0.899	0.809	0.868	0.812	0.885	0.871	0.819
Shape corrective factor (ϕ_f)	0.927	0.878	0.745	0.933	0.967	0.950	0.919	0.950
Roughness factor (ϕ_r)	1.166	1.078	1.017	1.201	1.315	1.228	1.158	1.311
Corrective factor (ϕ)	1.080	0.946	0.758	1.120	1.271	1.167	1.064	1.245
Surface area per unit mass (SA_m) [m^2/g]	0.0109	0.0111	0.0136	0.0054	0.0151	0.0039	0.0149	0.0205

Table 4. C, H, N and S contents of the CR samples.

		A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
C	(%)	77.00	77.10	79.22	78.83	78.26	76.21	81.89	81.54	78.37	77.05	81.50	82.10	81.50	84.40	80.80	81.60
H	(%)	7.24	7.02	7.34	7.16	7.38	7.00	7.23	7.25	7.03	7.09	7.42	7.41	7.35	7.55	7.27	7.61
N	(%)	0.52	0.51	0.47	0.48	0.49	0.53	0.48	0.39	0.46	0.43	0.43	0.42	0.54	0.37	0.46	0.43
S	(%)	2.14	1.86	2.02	1.98	2.42	2.22	2.33	1.69	2.03	1.96	1.86	1.80	1.95	1.84	2.14	1.48

Table 5. Metal contents of the CR samples.

		A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
Na	(mg/kg)	216	326	240	231	214	218	230	198	229	252	283	219	317	202	203	251
K	(mg/kg)	506	809	504	586	530	582	559	407	300	357	1514	738	1105	628	745	1030
Ca	(%)	0.349	0.411	0.364	0.546	0.180	0.357	0.345	0.496	0.130	1.120	0.181	0.268	0.276	0.235	0.382	0.354
Mg	(mg/kg)	444	719	350	542	397	999	445	1240	246	344	390	352	526	281	379	569
Fe	(%)	0.153	0.440	0.088	0.245	0.169	0.915	0.215	0.223	0.042	0.147	0.320	0.549	0.388	0.036	0.172	0.125
Mn	(mg/kg)	14.7	34.9	10.7	23.9	16.1	59.6	19.6	25.3	5.1	15.8	26.4	34.0	29.9	4.7	13.5	14.5
Ba	(mg/kg)	13.2	18.5	8.87	20.3	10.9	28.3	211.0	18.7	6.3	121.0	12.5	10.6	10.9	8.2	10.7	11.3
Al	(mg/kg)	630	1047	572	779	493	707	800	675	372	653	572	534	908	463	690	641
Cd	(mg/kg)	4.59	4.11	6.30	4.48	5.79	5.64	3.40	2.89	2.17	2.43	3.04	5.64	4.26	5.93	4.76	5.11
Cr	(mg/kg)	4.73	8.65	7.02	6.27	6.69	11.7	5.07	12.3	2.29	3.51	46.4	5.00	27.2	2.8	4.3	5.6
Ni	(mg/kg)	11.5	8.12	10.2	9.13	9.87	13.2	9.22	11.0	3.84	4.54	28.3	8.54	13.1	4.7	7.2	9.4
Pb	(mg/kg)	66.3	32.8	77.7	44.9	73.3	73.5	194.0	26.6	28.4	28.0	22.7	40.0	35.2	28.6	40.0	24.0
Cu	(mg/kg)	295	656	222	472	317	1218	353	80.0	64.3	85.9	118	149	447	32	298	73
Zn	(%)	2.03	1.21	1.94	1.83	2.10	2.26	1.87	1.33	1.16	1.18	1.41	1.50	1.35	1.34	1.54	1.25
Co	(mg/kg)	330	232	248	259	347	418	255	179	162	151	261	240	218	183	317	36.2
Ti	(mg/kg)	55.5	53.6	49.7	67.4	33.6	45.1	56.0	39.6	37.0	65.2	31.2	41.5	37.9	37.8	49.5	36.3
Sb	(mg/kg)	487	229	367	379	554	608	388	183	164	151	258	247	214	191	327	36.3

Table 6. VOC contents (in mg/kg) of the CR samples.

	A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
benzene	17.24	7.56	33.68	15.63	29.41	15.18	10.10	18.43	16.32	8.94	4.81	51.08	14.47	34.03	31.30	13.29
toluene	4.04	1.59	1.60	1.20	2.68	1.58	0.01	1.68	1.56	1.52	1.07	1.66	1.74	0.52	0.56	0.46
ethylbenzene	1.35	1.44	1.78	1.10	1.15	2.06	1.35	2.45	3.70	0.59	1.80	1.40	1.36	1.08	1.33	2.26
styrene	0.34	0.23	0.14	0.11	0.24	0.52	0.05	0.40	0.18	0.11	0.16	0.23	0.14	0.06	0.06	0.03
1,2,4-trimethylbenzene	4.77	0.82	2.84	2.44	1.60	1.65	1.80	4.08	2.78	2.84	1.24	5.50	0.88	0.94	0.97	0.92
1,3,5-trimethylbenzene	1.35	1.46	0.95	1.32	0.61	1.10	1.85	1.58	1.68	1.66	1.48	3.01	1.74	1.04	1.21	0.42
p-xylene	1.88	1.09	1.55	1.04	1.52	1.46	1.24	0.92	1.52	1.16	1.67	2.10	1.22	1.34	1.57	0.24
1,3,5-trichlorobenzene	5.84	1.25	3.02	3.64	3.20	1.19	4.43	1.56	4.53	3.44	1.14	5.61	2.30	0.94	0.97	0.92
1,2,4-trichlorobenzene	0.34	<0.001	<0.001	<0.001	0.33	<0.001	0.31	0.62	0.34	0.58	<0.001	0.760	<0.001	0.180	0.140	0.230
Total VOCs	37.15	15.44	45.56	26.48	40.74	24.74	21.14	31.72	32.61	20.84	13.37	71.35	23.85	40.13	38.11	18.77

Table 7. PAH contents (in mg/kg) of the CR samples.

	A 0.4-0.7	A 0.1-0.3	B 0.3-0.7	B 0.1-0.4	C 0.4-0.7	C 0.1-0.4	D 0.3-0.7	E 0.3-0.6	F 0.3-0.7	G 0.2-0.6	H 0-0.7	I 0.6-1.5	I 0.2-0.7	J 0.9-2.2	J 0.3-0.6	K 0.1-0.5
naphtalene	0.30	0.22	0.27	0.21	0.42	0.34	0.34	0.53	0.32	0.37	0.49	0.40	0.32	0.83	0.71	1.06
acenaphtylene	0.32	0.44	0.35	0.20	0.61	0.51	0.45	0.74	0.46	0.47	0.72	0.55	0.68	0.54	0.58	0.64
1-bromonaphtalene	0.03	0.02	0.05	0.05	0.07	0.06	0.06	0.02	0.06	0.05	0.02	0.16	0.01	0.12	0.07	0.13
acenaphtene	0.06	0.11	0.06	0.04	0.08	0.06	0.07	0.08	0.06	0.06	0.06	0.13	0.08	0.04	0.04	0.04
fluorene	0.02	0.28	0.16	0.12	0.22	0.21	0.20	0.28	0.19	0.21	0.12	0.35	0.02	0.21	0.17	0.03
phenantrene	2.80	2.84	1.45	1.56	1.90	1.84	1.68	3.36	1.54	2.27	1.88	3.38	1.80	4.15	4.36	1.20
anthracene	1.80	0.53	0.47	0.32	0.79	0.38	0.60	0.91	0.61	0.87	0.54	5.03	3.62	6.49	7.05	5.40
fluorantene	4.08	3.93	2.72	3.02	3.14	2.36	3.30	3.13	2.96	3.38	3.59	0.91	0.98	0.31	0.27	0.15
pyrene	13.12	12.51	10.02	10.52	11.30	17.20	12.46	16.04	11.29	10.92	10.46	17.90	13.30	18.43	24.73	9.09
benzo[a]anthracene	2.34	1.74	1.62	1.52	0.87	0.80	2.34	1.13	1.77	3.02	0.68	1.40	1.88	0.75	0.61	0.12
triphenylene	0.51	0.42	0.22	0.30	0.12	0.12	0.34	0.16	0.23	0.88	0.12	0.29	0.38	0.85	0.80	0.33
benzo[a]pyrene	0.85	0.60	0.85	0.45	0.47	1.22	1.22	0.61	1.02	1.85	0.45	0.41	1.06	1.91	2.67	0.53
benzo[b]fluorantene	0.94	0.58	0.67	0.48	0.31	1.21	0.96	1.43	0.76	1.56	0.31	0.59	0.76	1.67	2.83	1.08
dibenzo [a,h]anthracene	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
indeno[1,2,3-cd]pyrene	0.33	<0.001	0.19	0.15	0.10	0.20	0.12	0.14	0.10	0.19	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
benzo[ghi]perylene	3.68	1.52	3.11	1.82	1.35	0.84	3.62	2.04	3.54	4.56	0.80	2.63	2.60	2.99	3.25	0.34
Total PAHs	31.18	25.74	22.21	20.76	21.75	27.35	27.76	30.60	24.91	30.66	20.24	34.13	27.49	39.29	48.14	20.14

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