Action 2.5

Evaluation of the current status of the crumb rubber availability in Italy

POLITECNICO DI TORINO

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INTRODUCTION

Crumb rubber samples were taken from seven different treatment plants and were subjected to laboratory tests for the determination of particle size distribution and evaluation of content of heavy metals, PAH (polynuclear aromatic hydrocarbons), BTEX (benzene, toluene, ethylbenzene and xylene) and elemental analysis. Based on the combined analysis of available technical information and experimental data, it was possible to find relationships between the type of plant treatment and crumb rubber physical and chemical properties.

MATERIALS AND METHODS

Crumb rubber (CR)

The rubber matrix of tyres is constituted by a mixture of elastomers (natural and synthetic rubber) and several additives which include carbon black, plasticizers, vulcanisation accelerators, softeners and protecting additives (e.g. antioxidants and stabilizers). Natural rubber provides the tyre with its elastic properties, while synthetic rubber increases thermal stability characteristics. Even though tyre companies adopt their own specific formulations, it can be observed that in car tyres there is a greater percentage of synthetic rubber (mainly styrene-butadiene rubber), while truck tyres have a higher natural rubber content. Tables 1 show typical composition ranges of car and truck tyres, respectively referred to components and to main chemical elements.

Table 1. Typical composition ranges of car and truck tyres (components).

Component	Percent by weight	
	Cars	Trucks
Elastomers	46-48	41-45
Carbon black	25-28	21-23
Oils and zinc oxide	10-12	9-11
Steel	10-12	22-25
Textiles	3-6	-

Processing of ELTs for the production of CR is carried out in specialized plants where size-reduction operations are combined with other treatments (e.g. granulation, iron separation and sieving). The configuration of the plant can change significantly from case to case, and usually is a function of the actual inflow of material and of the desired quality of the end product.

Treatment processes of the seven plants which were considered in this action are synthetically described in Table 2. It can be observed that in most cases (plants 1, 3, 4, 5 and 6) the process is composed of four consecutive phases consisting in shredding, iron magnetic separation, milling and sieving. However, in two plants (2 and 7) shredding is carried out in two steps, with the possibility (as in the case of plant 2) of introducing an extra phase of iron separation in order to ensure a greater purity of the final CR product. Moreover, in one of the plants (number 2) size-reduction includes (plant 2) an intermediate cold granulation treatment which yields more cubical and uniformly shaped rubber particles fed to the milling unit. Finally, it is interesting to point out that plant 5 is equipped with a cryogenic system which allows low-temperature shredding and milling. According to owners, managers and operators, all the considered plants employ both car and truck tyres, with the only exception of plant 3, which collects exclusively ELTs coming from heavy vehicles.

Table 2. Description of treatment processes of the considered plants.

Phase	Treatment plant						
	1	2	3	4	5	6	7
Primary shredding	×	×	×	×	×*	×	×
Iron magnetic separation							×
Secondary shredding		×					×
Cold granulation		×					
Iron magnetic separation	×	×	×	×	×	×	×
Milling	×	×	×	×	×*	×	×
Sieving	×	×	×	×	×	×	×

(*) Carried out in cryogenic conditions.

CR samples were taken from all plants and were thereafter subjected to laboratory tests for the determination of particle size distribution, evaluation of content of heavy metals (Al, As, Ba, Cd, Co, total Cr, Cu, Fe, Mn, Ni, Pb, Sb,Ti, Zn), PAH (polynuclear aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene and xylene) and elemental analysis (C, H, N, S).

Particle size distribution analysis was performed by making use of sieves of the Tyler series in dry conditions.

Metals were determined by using a Perkin-Elmer Optima 2000 ICP-OES after a two-stage digestion in a Milestone 1200 Mega microwave oven in the presence of sulfuric acid (97%, Sigma Aldrich, 3 ml for 250 mg of sample, first stage) and nitric acid (65%, Sigma Aldrich, 3 ml for 250 mg of sample, second stage).

Analysis of BTEX and PAH was carried out by means of solvent extraction and subsequent gas-chromatographic analysis. A 2 g sample was extracted with 20 ml of CH_2Cl_2 kept for 20 minutes in microwave oven set at 600 W. Gas-chromatographic analyses were performed by using a GC-MS Agilent GCD 1800C, equipped with a J&W DB624 capillary column (J&W DB624, 30m×0.25mm×1.4μm) for BTEX and with a HP5-MS capillary column (HP5-MS, 30m×0.25mm×0.25μm) for PAH.

Carbon, hydrogen, nitrogen and sulphur contents were determined by employing a Flash 2000 ThermoFisher Scientific CHNS analyzer.

RESULTS

Tests on crumb rubber samples

Results of tests carried out for the physical and chemical characterization of CR samples are synthesized in Figure 1 (particle size distribution) and Tables 3 and 4 (chemical analyses).

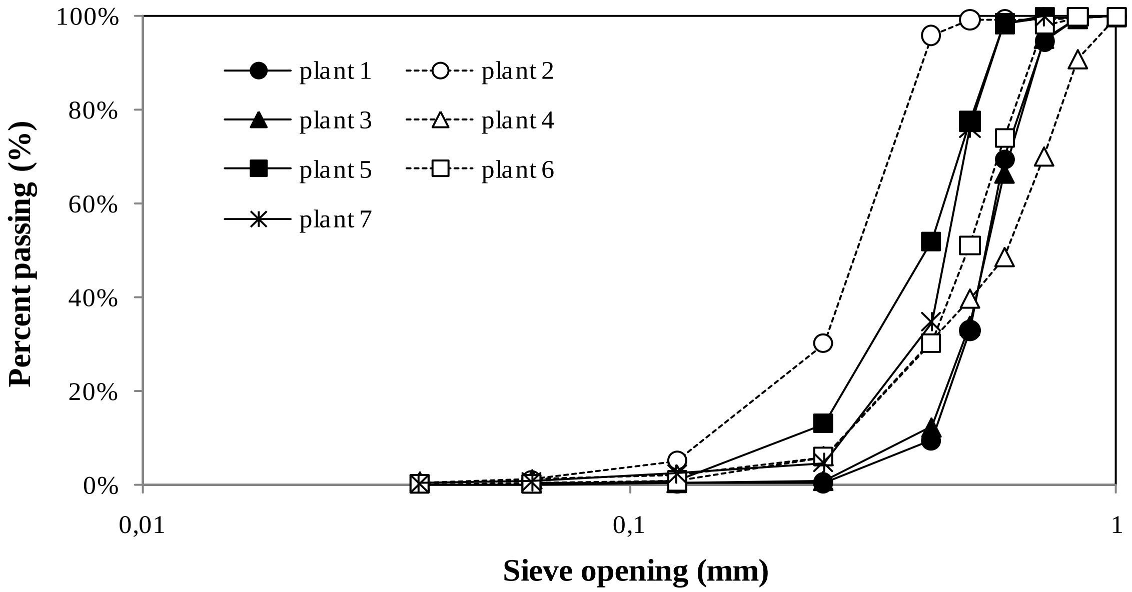

Figure 1. Particle size distribution of the seven CR samples.

Particle size distributions (Figure 1) highlight differences between the considered CR samples which are due to production processes (Table 2). In particular, samples taken from plants 2 and 5 are those which are finer and have a wider distribution. For the material produced by plant 2 this is possibly due to the fact that two shredding operations and one cold granulation are carried out. In the case of CR coming from plant 5 this is caused by the cryogenic conditions of treatment, which lead to the production of very fine a regularly-shaped particles.

It should be pointed out that size distributions are extremely important since they give an idea of the possible specific surface available for interaction with bitumen. Thus, it is generally considered that finer CRs may indeed show a greater affinity with the base bitumen.

Table 3. Metals and C, H, N, S content of the seven CR samples.

Element		Treatment plant						
		1	2	3	4	5	6	7
Na	(mg/kg)	216	231	214	230	252	229	198
K	(mg/kg)	506	586	530	559	357	300	407
Ca	(%)	0.349	0.546	0.180	0.345	1.12	0.130	0.496
Mg	(mg/kg)	444	542	397	445	344	246	1240
Fe	(%)	0.153	0.245	0.169	0.215	0.147	0.042	0.223
Mn	(mg/kg)	14.7	23.9	16.1	19,6	15.8	5.07	25.3
Ba	(mg/kg)	13.2	20.3	10.9	211	121	6.29	18.7
Al	(mg/kg)	630	779	493	800	653	372	675
Cd	(mg/kg)	4.59	4.48	5.79	3.40	2.43	2.17	2.89
Cr	(mg/kg)	4.73	6.27	6.69	5.07	3.51	2.29	12.3
Ni	(mg/kg)	11.5	9.13	9.87	9.22	4.54	3.84	11.0
Pb	(mg/kg)	66.3	44.9	73.3	194	28.0	28.4	26.6
Cu	(mg/kg)	295	472	317	353	85.9	64.3	80.0
Zn	(%)	2.03	1.83	2.10	1.87	1.18	.16	1.33
Co	(mg/kg)	330	259	347	255	151	162	179
Ti	(mg/kg)	55.5	67.4	33.6	56.0	65.2	37.0	39.6
Sb	(mg/kg)	487	379	554	388	151	164	183
C	(%)	77.03	78.83	78.26	81.89	77.05	78.37	81.41
H	(%)	7.23	7.16	7.38	7.23	7.09	7.03	7.47
N	(%)	0.52	0.48	0.49	0.49	0.43	0.46	0.46
S	(%)	2.14	1.99	2.42	2.33	1.96	2.03	1.90

With respect to heavy metals content, Table 3 shows that CR produced by plant 6 overall exhibits the lowest values, probably as a result of an efficient selection of materials. CR from plant 5 (cryogenic) has high calcium and barium contents. In the case of calcium this may be caused by calcium hydroxide which can be added in shredding operations to reduce rubber stickiness. Barium is also present in a high percentage in CR taken from plant 4.

When considering elemental analysis, results are quite uniform for all plants, thus revealing that the average composition of tyres is indeed constant. However, CRs sampled from plants 4 and 7 show a very high carbon content, which may be due to the addition in the treatment process of non-vulcanized rubber coming from alternative sources.

Table 4. Benzene and PAH content of the seven CR samples.

Compound	Treatment plant						
	1	2	3	4	5	6	7
Benzene (mg/kg)	17.24	15.63	29.41	10.10	8.94	16.32	
Naphtalene (mg/kg)	0.30	0.21	0.42	0.53	0.37	0.32	0.53
Phenantrene (mg/kg)	2.80	1.56	1.90	1.68	2.27	1.54	3.36
Anthracene (mg/kg)	1.80	0.60	0.79	0.32	0.87	0.61	0.91
Fluorantene (mg/kg)	4.08	3.02	3.14	3.30	3.38	2.96	3.13
Pyrene (mg/kg)	13.12	10.52	11.30	12.46	10.92	11.29	16.04
Benzo[a]anthracene (mg/kg)	2.34	1.52		2.34	3.02	1.77	1.13
Crysene (mg/kg)		0.30		0.34			0.16
Benzo[a]pyrene (mg/kg)				1.22	1.85	1.02	0.61
Benzo[b]fluorantene (mg/kg)							
Indeno[1,2,3-cd]pyrene(mg/kg)	0.33	0.15	0.10	0.12	0.19	0.10	0.14
Benzo[g,h,i]perylene(mg/kg)	3.68	1.82	1.35	3.62	3.11	3.54	2.04

Table 4 shows that BTEX and PAH values associated to the analyses performed on the sample taken from plant 3 are very low when compared to other considered materials. This specific result may be related to the practice followed in such a plant, fed exclusively by truck tyres which have a major percentage of natural rubber with a low content of organic aromatic substances. CR coming from the cryogenic plant (number 5) yields the maximum values of benzene and PAH. This is probably due to the fact that the low-temperature treatment does not allow volatilization of organic substances to take place to the same extent of ambient processing.

CONCLUSIONS

Based on the analysis of the characteristics of seven ELT treatment plants and on the results of investigations carried out on CRs and bituminous mixtures, several conclusions can be drawn.

There is a direct relationship between the type of plant treatment and particle size distribution of CR. In particular, in order to obtain fine CRs, characterized by a high specific surface which may promote CR-bitumen interactions, it may be convenient to include various size-reduction operations before milling (e.g. multiple shredding and intermediate granulation).
BTEX and PAH contents of CR are a function of the type of tyres which are fed to the treatment plant. If only truck tyres are accepted, a significant decrease of such environmental related parameters can be obtained.

Cryogenic treatment can be an option in order to obtain fine CRs. However, since resulting particles are extremely smooth, there may be compatibility problems with bitumen as a result of the low surface area. Moreover, CRs produced with this technology have higher values of BTEX and PAH contents, thus leading to a potentially lower environmental compatibility.

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