

Tests of Cement and Slag Mortars with SBR Rubber Granulates in Terms of Ecotoxicity and Strength

Beata GRYNKIEWICZ-BYLINA¹), Barbara SŁOMKA-SŁUPIK²), Bożena RAKWIC³)

¹⁾ KOMAG Institute of Mining Technology, Pszczyńska 37, 44-101 Gliwice, Poland; email: bbylina@komag.eu; ORCID ID: 0000-0002-6028-520X

²⁾ Faculty of Civil Engineering, Silesian University of Technology, Akademicka 5, 41-100 Gliwice, Poland; email: barbara.slomka-slupik@ polsl.pl; ORCID ID: 0000-0001-6112-4494

³⁾ KOMAG Institute of Mining Technology, Pszczyńska 37, 44-101 Gliwice, Poland; email: brakwic@komag.eu; ORCID ID: 0000-0002-9535-8886

http://doi.org/10.29227/IM-2023-02-71

Submission date: 21-11-2023 | Review date: 30-11-2023

Abstract

Various solutions for the management of rubber waste from used tires are known. We encounter in particular tests of concrete mixtures and the finished product, in the literature. These tests are describing rheological, mechanical and durability properties, mainly. However, the high toxicity of rubber waste from car tires requires that such concrete be tested in terms of ecotoxicology. The paper presents the results of research on the use of three different SBR granulates as fillers in mortars with a slag or CEM IV cement binder. The focus was on the immobilization of harmful compounds from rubber granules in the binder mass. It was assumed that the construction product using mortar with rubber granules would be in contact with water. The mass share of granulates in mortars was 4.7%. The grain size of the granulates was up to 4 mm, mainly 1–3 mm. A decrease in the strength of mortars with the addition of granulates and no leaching of polycyclic aromatic hydrocarbons from mortars was demonstrated. The metals from the mortars were absorbed by the rubber, most probably. The strength of slag mortars was greater than cement mortars.

Keywords: CEM IV, activated slag mortar, SBR rubber granulate, PAHs, toxicity, leaching

1. Introduction

Used car tires are a huge ecological problem due to their increasing quantity. Tires are made from rugged, hard-wearing rubber, so disposing of them is a major environmental challenge. They cannot be easily recycled, are difficult to reuse, break down into crumbs causing an increase in the content of microplastics in the environment [1-5]. Pilkington [2] emphasizes that the United States alone disposes of 246 million to 300 million used tires each year. Globally, the problem is quantified at between 1 billion and 1.8 billion used tires every year. This makes up between 2% and 3% of all the waste collected on Earth [2]. This problem will increase as the world's population grows - especially as the growing middle class population in poorer countries creates a larger market for personal transportation [2]. According to the report of the World Bank (2019) entitled "What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050" [6] an increase in waste generation of up to 70% was expected by 2050. From 2.01 billion tons in 2016, a total of 3.4 billion tons of annual waste was projected for the year 2050. Thus, the problem of tire waste disposal is quite serious. Due to the growing problem with waste tires worldwide, researchers are now focused on preparing rubberized concrete a widely used, greener construction material [2,3,7]. They combine with various binders shredded used tires as aggregate in varying degrees of filling and grinding, depending on the desired properties and designation [8]. Tire-derived aggregates (TDA) have been gaining more and more popularity in recent years [9]. Studies give different results. First research on rubberized concrete in the 1990s [8] found that the addition of rubber to a concrete

mixture decreased the material's flexural and compressive strengths. It was also shown that cracking in concrete occurred more frequently than in conventional concrete due to the poor adhesion between rubber materials and other components of the concrete [2].

On the other hand, researchers found that, compared with conventional concrete, rubberized concrete displayed high toughness, a good capacity for plastic energy, strong durability, low porosity, abrasion resistance, and low density. Recent advances in rubberized concrete studies (9-16) have found that, it displays better crack resistance than conventional concrete. This kind of concrete is also more resistant to tensile stresses than conventional concrete, and is relatively flexible, which means it can withstand heavy impacts more effectively [2,10]. Moreover it was also found that mechanical strength of concrete with the addition of rubber is improved by the use of silica fume [11]. An exemplary studies on the durability of concrete with the addition of rubber have shown that with 7.5% of the addition, less chloride penetration is obtained [9]. In most cases, concrete with rubber granulate was tested for strength, sorption and durability characteristics. Researchers were focusing on the effectiveness of binding the rubber to the binder as well [12-17].

However, there are few works that pay attention to the interaction of this concrete with the natural environment. Such concrete can be in contact with groundwater, rainwater, technological water, which can cause leaching of various compounds from it. This concrete will then be stored as demolition waste in landfills or used to strengthen the ground.

An example all-season van tire contains approximately 30 types of synthetic and 8 natural rubbers, 8 types of carbon



Tab. 1. Grain size of SBR granules, fraction share and photos of granulates on graph paper Tab. 1. Uziarnienie granulatów SBR, udział frakcji i fotografie granulatów na papierze milimetrowym

black and 40 different chemicals, waxes, oils, pigments, silica and clays [1,17–20]. According to ETRMA [19], tires contain an exemplary composition: rubber/elastomers (48%), carbon black (22%), metal (15%), additives (8%), textiles (5%), zinc oxide (1% passenger tires or 2% truck and off-road tyres), sulfur (1%). Ultimately, the tire consists of rubber, which accounts for about 70-80% of the tire weight, steel and textile fibers [21].

Literature data indicate that in recycled tire granulates there may be chemicals that are toxic to human health and the environment [22–30]. Their source may be raw materials of inadequate quality used to produce rubber mixtures or

Component	GGBFS	CEM IV
SiO ₂	40.43	32,99
CaO	43.27	34.88
Al ₂ O ₃	7.88	15.05
Na2O	0.46	0.41
Fe ₂ O ₃	0.81	4.57
MgO	6.97	1.56
K ₂ O	0.29	1.66
TiO ₂	0.28	ND
MnO	0.16	ND
P2O5	0.02	ND
Cr ₂ O ₃	0.01	ND
ZrO ₂	< 0.01	ND

Tab. 2. Chemical composition of cement and slag, %mas [*ND – not detected] Tab. 2. Skład chemiczny cementu i żużla, %mas [*ND – nie wykryto]

Tab. 3. Composition of mortar mixtures and volumes of SBR granules Tab. 3. Skład mieszanek zapraw i objętości granulatów SBR

Mortar	CEM IV, g	Water, g	Sand, g	Granulate, g	Granulate type	Bulk volume of granules, ml
GK-A	450	225	1350	0	-	-
GK-C	450	225	1350	100	SBR-C	175
GK-D	450	225	1350	100	SBR-D	160
GK-F	450	225	1350	100	SBR-F	200
Mortar	GGBFS, g	Activating water, g	Sand, g	Granulate, g	Granulate type	Bulk volume of granules, ml
GK-A'	450	240	1350	0	-	-
GK-C'	450	240	1350	100	SBR-C	175
GK-D'	450	240	1350	100	SBR-D	160
GK-F'	450	240	1350	100	SBR-F	200

Tab. 4. Concentration of PAHs and leachability of zinc from SBR granulates, mg/kg [*ND – not detected] Tab. 4. Zawartość wwa i wymywalność cynku z granulatów sbr, mg/kg [*ND – nie wykryto]

Cranulata		Zn loochohilitu						
Granulate	BghiP	Phenanthrene	Fluoranthene	PYR	Naphthalene			
SBR-C	4,67	2,14	7,32	16.4	0.000	2,38		
SBR-D	2.64	ND	ND	8.56	0.683	1.43		
SBR-F	4.84	1.50	6.09	19.6	0.538	2.66		

contamination of the rubber vulcanization process or tire recycling [31–33]. These substances include polycyclic aromatic hydrocarbons (PAHs) and heavy metals such as Pb, Cd, Hg, Cr, Zn and Sn. PAHs, Pb, Cd i Hg are classified according to Regulation (EC) No. 1272/2008 of the European Parliament and of the Council (EC) No. 1272/2008 – CLP, as substances that are carcinogenic and posing a threat to the aquatic environment [34].

The mentioned substances may be washed out and released into the environment with groundwater. After entering the environment, they do not biodegrade, accumulate in living organisms and may negatively affect their organs and systems [35]. Exemplary leaching tests carried out by Grynkiewicz-Bylina et al. [1] of 84 samples of rubber granulate taken from the surface of sports fields or delivered by recyclers in Poland indicated the excessive content of PAHs (polycyclic aromatic hydrocarbons) specified in the REACH Regulation [36].

Due to the lack of legal regulations specifying the criteria for assessing cement and slag mortars with rubber granulates in this work included criteria for admitting inert waste to landfills for heavy metals, including permissible limit values for their leaching set out in the Council Decision of 19 December 2002 [37]. The permissible leaching limits are as follows: Hg: 0.01 mg/kg; total Cr: 0.5 mg/kg; Zn: 4 mg/kg; Cd: 0.04 mg/kg; Pb: 0.5 mg/kg.

Harmful substances may also be present in blastfurnance slag, as indicated by research conducted by Giergiczna et. al [38].

For the above reasons, there is a belief that concrete with granulate is dangerous.

The gaps in testing the ecotoxicology of concrete with TDA are the reason for creating stereotypes that prevent the

use of such concrete in construction. De Maeijer et al. [17] after a detailed study of the literature in the field, noticed that there is little research on the ecotoxicological impact of rubber granulate, which represents a huge gap in knowledge.

A leaching study of 8 concrete mixtures with rubber granulate by Kardos and Durham [39] indicated that the concentration of both leached metals and volatile organic compounds was below acceptable limits. These concrete mixtures was made of Portland cement with fly ash and chemical admixtures. Other studies indicate that the reaction of the environment in which the rubber granulate is located can have a large impact on leaching. For example, trace metals can be more easily extracted from rubber under acidic conditions, and the amount of dissolved organic carbon increased significantly under alkaline conditions [17].

Therefore, it was decided that further tests of hardened mixtures of building binders with the use of these granules must be subjected to leaching tests of toxic chemical substances. The complex microstructure of the binder matrix can immobilize toxic metals [17,39].

In this work CEM IV and activated granulated blast furnace slag (GBFS) was used as a binders as a less emissive, to increase the ecological index on both sides. It is true that currently in Europe there is a trend of liquidation of blast furnace processes, but this research on a global scale is up to date.

Work [40] presents research using slag and tire granules in concrete, however, slag was used as a 20% binder substitute, and the basic binder was Ordinary Portland Cement (OPC). Akram et al. [40] replaced the natural aggregate with rubber granulate in the amount of 5, 10, 20 and 30% of the concrete volume. They investigated rheological, mechanical and dura-



Fig. 1. The sum of PAHs concentration in granulates (SBR-C to SBR-F), mg/kg Rys. 1. Suma zawartości WWA w granulatach (SBR-C do SBR-F), mg/kg



Fig. 2. Results of bending strength of cement mortars (G-KA to GK-F) and slag mortars (GK-A' to GK-F') Rys. 2. Wytrzymałość na zginanie zapraw cementowych (G-KA do GK-F) i żużlowych (GKA' do GK-F')

bility properties. They found that the strength decreases with the increase in the granule content due to the low cohesion of the rubber with the cement paste, and that the use of slag increased the resistance to acid attack. They calculated also that concrete with slag and rubber granules can be more efficient: it reduces workability, reduces flow, has lower CO₂ emission, lower costs, lower energy and water requirements. The exemplary strength of the samples tested at day 28 increased from 11.6% to 23.2, 34.8 and 39.5% with an increase in the degree of replacement from 5% to 10, 20 and 30%, respectively, relative to the not modified concrete samples with CEM I without rubber granules.

In work [41], in turn, the influence of the addition of styrene-butadiene copolymer (SBR) on the early hydration of cement was investigated. Studies have shown that the SBR copolymer delays the setting of cement.

2, Materials and Methods

The research began with verifying the type of material used to make samples of ground black rubber granules (GK-C, GK-D and GK-F) obtained from the recycler. For this purpose, the identification of plastic in rubber granules was carried out using the pyrolytic thermal desorption method coupled with gas chromatography with mass spectrometry detection (TD-Pyr GC-MS) according to [42], based on the presence of fragmentation products. This method was chosen, because it allows the identification of organic compounds directly from the sample without the long-term and labor-intensive preparation process, required in other methods, such as Raman microscopy (RM) or Fourier transform infrared spectroscopy (FTIR) [43].

The content of 15 PAHs was determined in the granulate samples: benzo[a]pyrene BaP, dibenz[a,h]anthracene DBA-

hA, benzo[e]pyrene BeP, benz[a]anthracene BaA, chrysene CHR, benzo[b]fluoranthene BbFA, benzo[j]fluoranthene BjFA, benzo[k]fluoranthene BkFA, indeno[1,2,3-cd]pyrene IcdP, benzo[ghi]perylene BghiP, phenanthrene, anthracene, fluoranthene, pyrene and naphthalene. The determination was performed by gas chromatography with tandem mass spectrometry (GC-MS/MS) using a gas chromatograph coupled with a GCMS/MS/7890B/7000C mass detector. This method was selected due to the high sensitivity and selectivity achieved for low levels of PAHs using GC-MS/MS compared to other commonly used analytical techniques such as high-performance liquid chromatography (HPLC) combined with a UV, fluorescence or diode-array detector (DAD).

The grain size analysis of 3 types of rubber granulates was performed on the basis of the ISO 13320:2009 [44] laser diffraction method. This method is applicable to particle sizes ranging from 0.1 μ m to 3 mm. The study was conducted in isopropanol using a Horiba LA-300 device. The results are presented in Table 1.

The ground granulated blast furnace slag had a specific surface area of 3850 cm2/g according to Blaine. The use of slag as a binder required the use of an alkaline activator, which was sodium metasilicate in an amount of 5% in relation to the weight of the slag, as in [45]. Using X-ray diffraction, it was confirmed that the slag contained approximately 98% of the amorphous phase. The cement marked CEM IV/B(V)32.5N is a pozzolanic cement, according to EN-197-1, with normal early strength, consisting of clinker (40-60%), silica fly ash (max. 55%) and gypsum (3–5%).

To determine chemical composition of cement and GGBFS grounded to a grain size less than 100 μ m and dried at 105°C to constant weight, the X-ray fluorescence method



Fig. 3. Results of compressive strength of cement mortars (G-KA to GK-F) and slag mortars (GK-A' to GK-F') Rys. 3. Wytrzymałość na ściskanie zapraw cementowych (G-KA do GK-F) i żużlowych (GKA' do GK-F')



Fig. 4. 4×4 cm fracture of the GK-D cement mortar beam after bending strength test with visible black SBR-D rubber granules Rys. 4. Przełam zaprawy cementowej GK-D po badaniu wytrzymałości na zginanie z widocznymi czarnymi granulami gumowymi SBR-D

(XRF) was used, according to PN-EN ISO 12677:2011 [46]. The chemical composition analysis was performed using a MagiX PW2424 spectrometer produced by PANalytical. The chemical composition of cement and slag is given in Table 2.

Then, mortar mixtures were made with the composition given in Table 3, using distilled water and standard sand with the trade name Kwarcmix (PN-EN 196-1).

The rubber granulate was mixed with sand first, and then the procedure was followed according to the rules of PN-EN 196-1. Bars measuring $4 \times 4 \times 16$ cm were formed. Mortars marked "A" did not contain granulates, and the remaining mortars contained SBR granules with similar grain sizes, and each of them was added to the mortar in the same mass quantity. The bulk volumes of the granulates were different, as shown in Table 3. After demoulding, the mortar bars were conditioned at a temperature of $20\pm2^{\circ}$ C and protected against moisture loss. The strength test was carried out in accordance with the standard [47]. Cement mortars were tested after 28 days, and slag mortars were tested after 14 days.

The leachability of harmful substances was tested for granules and for mortars after 2 months of hardening.

The leachability of the following metals was determined in the granulates: Hg, total chromium (Cr) and hexavalent (Cr(VI)), Zn, Cd, Sn and Pb. The leachability of 15 PAHs was determined in mortars. Content of PAHs in granulates was tested, as well.

Shredded samples of SBR granulates and mortars were dynamically washed with deionized water according to PN-EN 12457-4:2006 [48]. The pH value of the water used for leaching did not exceed 6.7.

Determination of leachability of elements: total Cr, Zn, Cd, Sn, Pb from mortars was carried out by the inductively coupled plasma mass spectrometry (ICP-MS) method with the use of Agilent 7900 ICP-MS. This method is characterized by a low limit of quantification and high selectivity, which enables the simultaneous determination of many elements in complex matrices, such as trace amounts of rare earth elements (REE) in waste [49].

The leachability of Cr(VI) from rubber granules was determined by high-performance liquid chromatography with inductively coupled plasma mass spectrometry (HPLC-ICP-MS) using Agilent 7700 Series ICP-MS with Agilent 1260 Infinity series HPLC.

Cold-vapor atomic absorption spectroscopy (CV-AAS) with the Perkin Elmer FIMS 100 mercury analyser was selected for the Hg leaching study due to the use of a unique technique of mercury vapour measurement at room temperature.

The leachability of PAHs from mortars was determined by gas chromatography with tandem mass spectrometry [GC-MS/MS] used to determine the PAH content in granulates, as well.

3. Results

Plastic identification results. The tests carried out using the TD-Pyr GC-MS method showed in granulate samples the presence of: 1,3-butadiene, toluene (TO), 4-vinylicyclohexene (D), styrene (S), α -methylstyrene, C12H18 (B trimer), C12H14 (SB hybrid dimer), C16H12 (SBB hybrid dimer), which are SBR fragmentation products. Therefore, based on the obtained test results, it was found that the used granulates are SBR, i.e. styrene-butadiene rubber used for the production of tires in the vulcanization process.

The results of testing the PAH content in rubber granulates given in Table 4, include values other than zero only. The sums of PAHs content in granulates are shown in Figure 1. Analyzing the above results, it can be concluded that the tested granulates contained 3 to 5 PAHs (BghiP, phenanthrene, fluoranthene, PYR, naphthalene). The highest total PAH content was recorded for SBR-F granules (32.6 mg/kg) and the lowest for SBR-D granules (11.9 mg/kg).

Mortar	Hg	Cr(VI)	Cr _{total}	Zn	Cd	Sn	Pb
GK-A	0.00100	0.000080	0.0233	nd	nd	nd	0.0767
GK-C	0.00095	nd	nd	nd	nd	nd	0.0367
GK-D	nd	nd	nd	nd	nd	nd	0.0333
GK-F	nd	nd	nd	nd	nd	nd	0.0433
GK-A'	-	nd	nd	0.283	nd	nd	nd
GK-C'	-	nd	nd	nd	nd	nd	nd
GK-D'	-	nd	nd	nd	nd	nd	nd
GK-F'	-	nd	nd	nd	nd	nd	nd

Tab. 5. Leachability of metals from mortars, mg/kg [*nd – not detected] Tab. 5. Wymywalność metali z zapraw, mg/kg [*nd – nie wykryto]

The results of testing the grain size of rubber granulates are presented in Table 1. As can be seen, the granulate called SBR-C has the largest granulation, and SBR-F the smallest granulation, and therefore the largest specific surface, which could not be determined due to the no stiffness of the matrix. SBR-D and SBR-F granules have dimensions in the range of 1.0–2.0 mm (approx. 80%), while SBR-C granules had dimensions of 1.0–4.0 mm (90%).

When comparing the chemical composition of cement and slag, one can notice a great similarity in composition. There was slightly more aluminum in the cement, by about 7%, while the slag binder contained more magnesium, silicon and sodium (due to the use of an activator after mixing).

The results of the mortar strength test are presented in Figure 2 and Figure 3. Slag mortars have the prime symbol. The research shows that although the hardening time of cement mortars was longer, they obtained lower strength than slag mortars. The addition of granules in the amount of 7.4% by mass compared to the mixture, contributed to a reduction in flexural and compressive strength for each mixture. Bending strength of slag mortars decreased by about 20–40% and the compressive strength by about 20–36%. In turn, in the case of cement mortars, the bending strength decreased by approximately 18–80% and the compressive strength by approximately 40–70%. It should be additionally emphasized that after breaking the bars, it was difficult to separate its halves. This proves good adhesion of rubber granules to binders.

The quality of the granules had a significant impact on the mechanical properties of mortars. Granules made of rubber with the highest density (SBR-D) and the smallest grain size variation had the lowest bending strength value. Probably due to their compact microstructure, they were least consistent with the binder matrix. In contrast to SBR-C granules, the grain size of which was more varied and included even a 3-4 mm fraction. The cement mortar that achieved the highest strength, both in bending and compression, was the one using the smallest granules (SBR-F). This was most likely due to their large number and the most developed specific surface. However, the slag mortar worked best with SBR-C granules, and this mixture (GK-C') achieved the highest strength values of all mixtures with SBR granules.

Figure 4 shows a photo of an exemplary fracture of the GK-D cement mortar beam with visible rubber granules.

The results of the leachability of harmful substances from granules and mortars are presented in Tables 4 and 5.

Despite many tests described in the point above, Tables 4 and 5 include only those values that were partly different from zero in a given series of determinations. In the remain-

ing examinations, the compounds were not detected or were at the detection level. The most frequently leached metal from SBR granules was zinc, which is the first to be responsible for the increased toxicity of leachates from used tire granules [17] because it is used as a vulcanization activator. Among determined metals: total Cr, Zn, Cd, Sn, Pb, Cr(VI) and Hg, only Zn was washed from the granulates, and additionally Hg, Cr(VI), total Cr and Pb were washed from the mortars. Therefore, these elements came from binders.

Referring the obtained test results to the permissible limit values for metal leaching for inert waste permitted for storage in inert waste landfills [37], no exceedances were found for mortars.

It should be noted here, the work focuses on investigating the toxicity caused by the rubber granulates, and the results show that the granulates contributed to the reduction the leachability of metals. This was most likely due to the sorption properties of the granules. Only mercury present in the cement mortar GK-A was also present in the mortar with granules (GK-C). The amount of Pb washed from cement mortars was reduced by approximately 60-40% thanks to the use of rubber granules.

PAHs contained in SBR granules, including BghiP, phenanthrene, fluoranthene, PYR, naphthalene, were not washed out of the mortars.

4. Summary

The key feature of rubberized concrete is its huge potential for environmental benefit. There are few solutions available for the growing tire waste problem. Thus the rubberized concrete may be a viable way to close this large waste loop. Granulated concrete has a number of desirable properties such as lower density, higher durability and higher impact resistance compared to conventional concrete. The flexibility of concrete with rubber granulate dedicates it to impact-absorbing applications. So it can be used as shock absorber in road construction and as earthquake wave damper in buildings [6]. Concrete with rubber granules is also a good sound absorber. Rubber granulate concrete is very well suited for the production of footings and slabs, which, for example, in Australia makes up 40% of all concrete consumption [2].

Test results indicate that the granules in the mixture reduce the strength, which in turn will require the use of a higher-strength binder. Therefore, each time the design of concrete should be individually approached depending on its application.

We also need to work on special methods of preparing granules to optimize a composition of such kind of concrete and its manufacturing processes. Pretreating of rubber particles with chemical or mechanical treatments could improve cohesion with concrete particles and result in a stronger final material.

In a further stage of research, it is also planned to check the effectiveness of sorption of salts and mineral impurities in external plasters thanks to the addition of SBR or EPDM granules. It is also assumed to check the impact of granules in the mortar on the environment during a fire. Another research goal is to examine odorous compounds released from granulates and mortars containing granulates. To confirm the lack of ecotoxicity of mortars with rubber granules containing PAHs, due to the low solubility of these compounds in deionized water, which is the standard leaching liquid, it is planned, as part of further research, to leach them using a liquid simulating the chemical composition of the liquid in pores of mortars, i.e. strong bases and water activating the slag.

5. Conclusions

The results of the tests confirm the possibility of using rubber granulates in construction mortars. The mortars are not harmful to the environment. SBR granules make the mortar matrix coherent and do not separate under the influence of external forces.

The use of a filler in the form of rubber granules, in the amount of 4.7% of the total mass, reduced the strength of both cement and slag mortars. Slag mortars were characterized by greater durability.

Granules, not much different at first glance, turned out to have different properties. Therefore, rubber granulate collected even from one recycler cannot be treated in the same way due to different processing methods, types of tires and their wear. This is visible in the case of SBR-C granulate, which cooperated best with the slag binder, obtaining the highest strength, and in the case of SBR-F granulate, which provided the highest strength in the cement binder, but only in bending.

The aim of the study was to check the toxicity of rubber granules, but metals contained in the cement binder were absorbed by the granules. The mortars themselves turned out to be non-toxic. This allows us to claim that the granules contribute to increase environmental friendliness of mortars with rubber granules.

Conducting chemical analyzes for toxicity assessment purposes requires the use of advanced analytical techniques characterized by high sensitivity and low detection limits, due to the trace amounts of the chemical substances being determined.

Polycyclic aromatic hydrocarbons present in the SBR granulates were not detected in the mortar filtrates.

The lowest content of PAHs in SBR-D granules and the lowest strength of mortars with this granulate suggest the existence of a relationship. These relationships cannot be ruled out, but they cannot be confirmed at this stage of research, as well.

Literatura - References

- B. Grynkiewicz-Bylina, B. Rakwic, B. Słomka-Słupik, Tests of rubber granules used as artificial turf for football fields in terms of toxicity to human health and the environment. Sci. Rep. 12, 6683 (2022). https://doi.org/10.1038/ s41598-022-10691-1
- 2. B. Pilkington, A Closer Look at Mixing Rubber into Concrete. Available from 12-May-2022. https://www.azobuild. com/article.aspx?ArticleID=8543
- 3. B. Pilkington, Tackling the Global Tire Waste Problem with Pretred. (2021). AZO CleanTech. Available online at: https://www.azocleantech.com/article.aspx?ArticleID=1227
- 4. European Chemicals Agency ECHA. Opinion on an Annex XV Dossier Proposing Restrictions on Intentionally-Added Microplastics. Committee for Risk Assessment (RAC), Committee for Socio-economic Analysis (SEAC). ECHA/RAC/RES-O-0000006790-71-01/F, ECHA/SEAC/RES-O-0000006901-74-01/F (2020).
- S. Wagner, T. Hüffer, P. Klöckner, M. Wehrhahn, T. Hofmann, T. Reemtsma, Tire wear particles in the aquatic environment A review on generation, analysis, occurrence, fate and effects. Water Res. 139, 83-100 (2018). https://doi.org/10.1016/j.watres.2018.03.051
- 6. World Bank report "What a Waste 2.0: A Global Snapshot of Solid Waste Management to 2050" (World Bank, 2019). https://openknowledge.worldbank.org/server/api/core/bitstreams/92a50475-3878-5984-829e-0a09a6a9badc/content
- J. Xue, M. Shinozuka. Rubberized concrete: A green structural material with enhanced energy-dissipation capability. Constr. Build. Mater 42, 196-204 (2013). https://www.sciencedirect.com/science/article/pii/ S0950061813000688?via%3Dihub
- 8. A. Al-Balhawi, N.J. Muhammed, H.A. Mushatat, H.N.G. Al-Maliki, B. Zhang, Numerical Simulations on the Flexural Responses of Rubberised Concrete. Buildings 12(5):590 (2022). https://doi.org/10.3390/buildings12050590
- Z. Zarhri, W.R. Martinez, J.A.D. Lepe, R.E.V. Azamar, M.C. Juarez, B.B.P. Solis, 30 years of rubberized concrete investigations (1990-2020). A bibliometric analysis, Revista ALCONPAT 12 (1), 127-142 (2022). https://doi. org/10.21041/ra.v12i1.554
- 10. N.N. Gerges, C.A. Issa, S.A. Fawaz, Rubber concrete: Mechanical and dynamical properties. Case Studies in Con. Mater. 9, e00184, ISSN 2214-5095 (2018). https://doi.org/10.1016/j.cscm.2018.e00184.
- 11. B.H.A. Aleem, A.A.A. Hassan, Development of self-consolidating rubberized concrete incorporating silica fume, Constr. Build. Mater. 161, 389-397, ISSN 0950-0618 (2018). https://doi.org/10.1016/j.conbuildmat.2017.11.146
- 12. Y. Jiang, S. Zhang, G. Xue, W. Wang, Compressive behavior of rubberized concrete under high strain rates. Structures 56, 104983, ISSN 2352-0124 (2023). https://doi.org/10.1016/j.istruc.2023.104983
- N. Yasser, A. Abdelrahman, M. Kohail, A. Moustafa, Experimental investigation of durability properties of rubberized concrete. Ain Shams Eng. Journal 14, 6, 102111, ISSN 2090-4479 (2023). https://doi.org/10.1016/j. asej.2022.102111
- D.F. Medina, C.H. Martínez, N.F. Medina, F. Hernández-Olivares, Durability of rubberized concrete with recycled steel fibers from tyre recycling in aggresive environments. Con. Build. Mater. 400, 132619 ISSN 0950-0618 (2023). https://doi.org/10.1016/j.conbuildmat.2023.132619
- Q. Guan, Y. Xu, J. Wang, Q.Wu, P. Zhang, Meso-scale fracture modelling and fracture properties of rubber concrete considering initial defects. Theoretical and Applied Fracture Mechanics 125, 103834, ISSN 0167-8442 (2023). https://doi.org/10.1016/j.tafmec.2023.103834
- H. Momotaz, M.M. Rahman, M.R. Karim, Y. Zhuge, X. Ma, P. Levett, Properties of the interfacial transition zone in rubberised concrete – an investigation using nano-indentation and EDS analysis. J. Build. Enging. 77, 107405, ISSN 2352-7102 (2023). https://doi.org/10.1016/j.jobe.2023.107405
- 17. P.K. Maeijer, B. Craeye, J. Blom, L. Bervoets, Crumb Rubber in Concrete—The Barriers for Application in the Construction Industry. Infrastructures 6, 116 (2021). https://doi.org/10.3390/Infrastructures6080116
- V. Lapkovskis, V. Mironovs, A. Kasperovich, V. Myadelets, D. Goljandin, Crumb Rubber as a Secondary Raw Material from Waste Rubber: A Short Review of End-Of-Life Mechanical Processing Methods. Recycling 5, 32 (2020). https://doi.org/10.3390/recycling5040032
- 19. ETRMA. European Tyre and Rubber Industry-Statistics; ETRMA: Brussels, Belgium, 2014.
- A. Kailash, V. Mrudul, M. Tajedini, P. G. Xavier, E. Bardasz, M.J. Green, H.Liang, Impacts of particles released from vehicles on environment and health. Tribology International 184, 108417 (2023). ISSN 0301-679X. https://doi. org/10.1016/j.triboint.2023.108417
- 21. M. Sienkiewicz, J. Kucinska-Lipka, H. Janik, A. Balas, Progress in used tyres management in the European Union: A review. Waste Management 32, 10, 1742-1751 (2012). ISSN 0956-053X. https://doi.org/10.1016/j.wasman.2012.05.010

- 22. B. Bocca, G. Forte, F. Petrucci, S. Costantini, P. Izzo, Metals contained and leached from rubber granulates used in synthetic turf areas. Science of The Total Environment 407(7), 2183-2190 (2009). https://doi.org/10.1016/j.scito-tenv.2008.12.026
- 23. M. Beausoleil, K. Price, C. Muller, Chemicals in outdoor artificial turf: A health risk for users. Public Health Branch. Montreal Health and Social Services Agency (2009). https://ncceh.ca/sites/default/files/Outdoor_Artificial_Turf.pdf
- E. Menichini, V. Abate, L. Attias, S. De Luca, A. di Domenico, I. Fochi, G. Forte, N. Iacovella, A. L. Iamiceli, P. Izzo, F. Merli, B. Bocca, Artificial-turf playing fields: Contents of metals, PAHs, PCBs, PCDDs and PCDFs, inhalation exposure to PAHs and related preliminary risk assessment. Science of the Total Environment 409, 23, 4950-4957 (2011). https://doi.org/10.1016/j.scitotenv.2011.07.042 (2011).
- F.P. Gomes, H.I. Mota, J.C.M. Bordado, M. Baião, G.M. Sarmento, J. Fernandes, V.M. Pampulim, M.L. Custódio, I. Veloso, Toxicological Assessment of Coated versus Uncoated Rubber Granulates Obtained from Used Tires for Use in Sport Facilities. Journal of the Air & Waste Management Association 60, 741–746 (2012). https://doi. org/10.3155/1047-3289.60.6.741
- 26. M. Llompart, L. Sanchez-Prado, J. P. Lamas, C. Garcia-Jares, E. Roca, T. Dagnac, Hazardous organic chemicals in rubber recycled tire playgrounds and pavers, Chemosphere 90, 423-431 (2013). https://doi.org/10.1016/j.chemosphere.2012.07.053
- 27. A. Niesłochowski, H. Deptuła, Environmental tests of playground surfaces containing recycled rubber granulate. Przegląd Budowlany 10, 41-44 (2017), in Polish. http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-0b10a26c-5877-4dd2-93cc-0fb4d0c1783c
- M. Celeiro, T. Dagnac, M. Llompart, Determination of priority and other hazardous substances in football fields of synthetic turf by gas chromatography-mass spectrometry: A health and environmental concern. Chemosphere 195, 201-211 (2018). https://doi.org/10.1016/j.chemosphere.2017.12.063
- 29. A.N. Perkins, S.H. Inayat-Hussain, N.C. Deziel, C.H. Johnson, S.S. Ferguson, R. Garcia-Milian, D. C. Thompson, V. Vasiliou, Evaluation of potential carcinogenicity of organic chemicals in synthetic turf crumb rubber. Environmental Research 169, 163–172 (2019). https://doi.org/10.1016/j.envres.2018.10.018
- F.O. Gomes, M.R. Rocha, A. Alves, N. Ratola, A review of potentially harmful chemicals in crumb rubber used in synthetic football pitches. Journal of Hazardous Materials 409, 124998, ISSN 0304-3894 (2021). https://doi. org/10.1016/j.jhazmat.2020.124998
- 31. ECHA, Annex XV Report. An evaluation of the possible health risks of recycled rubber granules used as infill in synthetic turf sports fields. version 1.01. European Chemicals Agency (2017) https://echa.europa.eu/documents/10162/13563/annex-xv_report_rubber_granules_en.pdf/dbcb4ee6-1c65-af35-7a18-f6ac1ac29fe4
- A. Re Depaolini, G. Bianchi, D. Fornai, A. Cardelli, M. Badalassi, C. Cardelli, E. Davoli, Physical and chemical characterization of representative samples of recycled rubber from end-of-life tires. Chemosphere 184, 1320-1326 (2017). https://doi.org/10.1016/j.chemosphere.2017.06.093
- 33. K. Formela, Waste tire rubber-based materials: Processing, performance properties and development strategies, Advanced Industrial and Engineering Polymer Research 5, 234-247 (2022). https://doi.org/10.1016/j.aiepr.2022.06.003
- European Parliament, Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006, OJ L 353, 31.12.2008, p. 1-1355 with further amendments, http://publications.europa.eu/resource/cellar/e3f31046-b274-11eb-8aca-01aa75e-d71a1.0013.02/DOC_1 (accessed on 3 October 2023)
- 35. A. Ociepa-Kubicka, Toxic effects of heavy metals on plants, animals and humans, Engineering and Environmental Protection 15, 2, 169-180 (2012), in Polish. http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-ar-ticle-LODD-0002-0015
- 36. European Parliament, Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC, OJ L 396 30.12.2006, p. 1 with further amendments, https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:02006R1907-20230806 (accessed on 3 October 2023)
- 37. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC, OJ L 011, 16.01.2003 p. 0027 – 0049, https:// eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:32003D0033&qid=1696348429653 (accessed on 3 October 2023).

- E. Giergiczny, K. Góralna, Mielony granulowany żużel wielkopiecowy dodatek do betonu typu II. Budownictwo Technologie Architektura 1 56-59 (2008). http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-BTB2-0059-0097
- A.J. Kardos, S.A. Durham, Strength, durability, and environmental properties of concrete utilizing recycled tire particles for pavement applications. Con. Build. Mater. 98, 832-845 (2015). ISSN 0950-0618. https://doi.org/10.1016/j. conbuildmat.2015.08.065
- 40. A.M. Mhaya , G.F. Huseien, A.R. Z. Abidin, M. Ismail, Long-term mechanical and durable properties of waste tires rubber crumbs replaced GBFS modified concretes. Con. Build. Mater. 256, 119505 (2020). https://doi.org/10.1016/j. conbuildmat.2020.119505
- 41. R. Wang, X. Shi, Influence of styrene-butadiene rubber latex on the early hydration of cement. Cement Wapno Beton 21/83, 1, 36-45 (2016). http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-de8defdf-2500-4a91-a30f-11fcfe4044fd?q=49062ca2-624b-4dc7-84f7-ee6233e45929\$4&qt=IN_PAGE
- 42. S. Tsuge H. Ohtani, W. Chuichi, Pyrolysis-GC/MS data book of synthetic polymers Programs, Thermograms and MS of Pyrolyzates, 1st Edition, 2011.
- 43. J. Reichel, J. Graßmann, T. Letzel, J. E. Drewes, Systematic Development of a Simultaneous Determination of Plastic Particle Identity and Adsorbed Organic Compounds by Thermodesorption-Pyrolysis GC/MS (TD-Pyr-GC/MS). Molecules Oct 28;25(21), 4985 (2020). doi: 10.3390/molecules25214985. PMID: 33126488
- 44. ISO 13320:2009 Particle size analysis-Laser diffraction methods. Publication date: 2009-10. Technical Committee: ISO/TC 24/SC 4 Particle characterization. ICS: 19.120 Particle size analysis. Sieving. Available online: https://www.iso.org/standard/44929.html (accessed on 6 January 2020).
- 45. B. Słomka-Słupik, Self-Immobilizing Metals Binder for Construction Made of Activated Metallurgical Slag, Slag from Lignite Coal Combustion and Ash from Biomass Combustion. Materials 14, 3101 (2021) https://doi. org/10.3390/ma14113101.
- 46. PN-EN ISO 12677:2011 Chemical Analysis of Refractory Products By X-Ray Fluorescence (XRF)-Fused Cast-Bead Method; PKN: Warsaw, Poland, 2011.
- 47. PN-EN 196-1:2016-07 Metody badania cementu Część 1: Oznaczanie Wytrzymałości (Cement Test Methods-Part 1: Determination of Strength); PKN: Warsaw, Poland, 2018.
- 48. PN-EN 12457-4:2006 Charakteryzowanie odpadów -- Wymywanie -- Badanie zgodności w odniesieniu do wymywania ziarnistych materiałów odpadowych i osadów -- Część 4. PKN: Warszawa, 2006
- 49. R. Baron, Determination of rare earth elements in power plant wastes, Min. Mach. 4, 164, 24-30 (2020) DOI 10.32056/KOMAG2020.4.3

Badania zapraw cementowych i żużlowych z granulatami gumowymi SBR pod względem ekotoksykologiczności i wytrzymałości

Znane są różne rozwiązania zagospodarowania odpadów gumowych pochodzących ze zużytych opon, w literaturze napotykamy w szczególności na badania mieszanek betonowych i już gotowego wyrobu. Są to badania opisujące głównie właściwości reologiczne, mechaniczne i trwałościowe.

Jednak duża toksyczność gumowych odpadów z opon samochodowych nakazuje badać taki beton pod względem ekotoksykologicznym. W pracy przedstawiono wyniki badań nad użyciem 3 różnych granulatów jako wypełniaczy zapraw ze spoiwem żużlowym lub cementowym CEM IV. Skupiono się na immobilizacji szkodliwych związków z granul gumowych w masie spoiwa. Założono, że wyrób budowlany z użyciem zaprawy z granulatem gumowym będzie miał kontakt z wodą. Masowy udział granulatów w zaprawach wynosił 4,7%. Uziarnienie granulatów wynosiło do 4 mm, głównie 1–3 mm.

Wykazano spadek wytrzymałości zapraw z dodatkiem granulatów oraz brak wymywania wielopierścieniowych węglowodorów aromatycznych z zapraw. Metale z zapraw zostały zasorbowane przez gumę, w większości przypadków.

Słowa kluczowe granulat gumowy SBR, WWA, toksyczność, wymywanie, CEM IV, żużel