

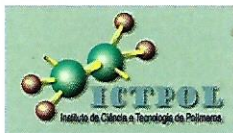
CERTIFICATE OF ANALYSIS

**Lab determination of PAH Content in rubber infill, and
Measurements of *In Vitro* PAH Migration to Artificial Sweat
– Skin exposure assessment on the contact by rubber infill**

- *A contribution to overcome the “PAH Restriction”* -

**Quantification of the Migration of Polycyclic Aromatic
Hydrocarbons (PAHs) from recycled rubber granulates
from end-of-life tyres when exposed to Artificial Sweat,
and comparison with existing contents of same PAHs in
granulates**

December 2019



Objective

Study of the Migration of Polycyclic Aromatic Hydrocarbons (PAHs) from recycled rubber granulates from end of-life tyres when exposed to Artificial Sweat, when compared to the existing contents of the same PAHs in rubber granulates. The samples were tested for 8 PAHs: Benzo[a]Pyrene, Benzo[e]Pyrene, Benzo[a]Anthracene, Chrysene, Benzo[b]Fluoranthene, Benzo[j]Fluoranthene, Benzo[k]Fluoranthene and DiBenzo[a,h]Anthracene.

This study was decided by the Portuguese Technical Commission CT-181 – “Recycled products from Tyres”, considering the very significant international market acceptance of the rubber infill produced in Portugal by the 3 Tyre Recycling Companies - “Recipneu”, “BioSafe”, “Biogoma” - as a technical contribution to overcome the “PAH Restriction”, and it was ordered to ICTPOL (“Institute of Science and Technology of Polymers”, integrated in the IST – Technical University of Lisbon) as a technical contribution for the evaluation of eventual health risks caused by PAHs of crumb rubber, in the situation of dermal contact of rubber infill with the skin of football players during the games played in synthetic turf football fields.

The methodology for this study was based in the excellent work of Nils H. Nilsson, Anders Feilberg and Kirsten Pommer, from the Danish Technological Institute, “*Emissions and evaluation of health effects of PAH's and aromatic amines from tyres*”, work ordered by the Danish Ministry of the Environment, Survey of Chemical Substances in Consumer Products, no. 54, 2005. This important paper is also presented as attachment.

The considered formula for the artificial sweat followed the composition given in ISO 105-E04:2013(E).

Sample collection



Identification: Portuguese tyre recycler; Tested ELT granulates; Particle size interval; Grinding technology

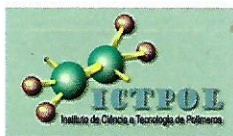
Tyre recycler	Tested ELT rubber granulate for rubber infill supplies	Nominal particle size interval	Technology used in the ELTs grinding process
Recipneu	Cryoflex® DC-0725 <i>cryogenic rubber infill</i>	[0.5 – 2.5 mm]	Cryogenic process - primary system
BioSafe	BIORG 0.8-2.5mm	[0.8 – 2.5 mm]	“Ambient”/ Mechanical process
Biogoma	G8TA100825	[0.8 – 2.5 mm]	“Ambient”/ Mechanical process

Sample Preparation for Content Determination

The method used was according to ‘AfPS GS 2014:01 PAH specification’. The sample considered was 2grams, and the initial amount of dichloromethane was 20mL (identical ratio to the one used in the migration determination). The rest of the procedure was adjusted accordingly.

Sample Preparation for Migration Determination

The sample preparation was based on the scientific work from Nils H. Nilsson (mentioned earlier) and the migration experiments used the formula for the artificial sweat given in ISO 105-E04:2013(E). The contact time, at 37°C, was of 2.5 hours, under slow constant stirring. The artificial sweats used had the pH value brought to pH 8 and pH 5.5, as required by the ISO standard. The rubber granulate sample considered was 10grams, placed in contact with 100mL of artificial sweat.



HPLC-Fluorescence (migration) and GC-MS (content) analysis

Based on the NIOSH, 1998. Polynuclear Aromatic Hydrocarbons by HPLC: METHOD 5506, NIOSH Manual of Analytical Methods (NMAM), fourth ed., the HPLC analyses for the determination of the migration content were performed using a HPLC chromatography unit with a fluorescence detector. Regarding the quantification of the PAH content in the rubber infill, the analytical technique used was GC with MS detection.

Results

The results are presented in the tables below, shown in the next two pages. Notice that for the migration results, all the PAHs compounds under study were separated chromatographically; for the content results, the compounds are grouped since the retention time is similar and thus the indicated value is the sum of the concentration of all the compounds in the group. The individual response factors of the detector regarding each compound were measured using standards and such factors are nearly the same for all the compounds.

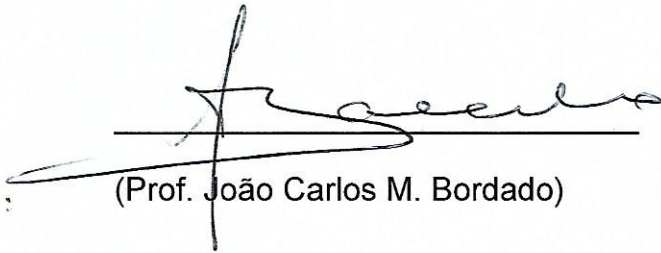
Conclusions

As expected, the **content** of PAHs in the rubber granulate is low, and the **migration** to artificial sweat is even lower, and in most cases bellow the detection limit. Taking into account that for human health the important factor has to do with the dermal contact of said compounds it is concluded that the hazard based on the migration data is negligible.

Accordingly to the recent document "EuRIC - Synthetic Turf Pitches and PAHs - Q&A Document on the Presence of PAH in Synthetic Turfs", where it is stated that "the analysis of 1.373 samples (*of "rubber infill" collected from existing synthetic turf pitches*) all across Europe determined that the presence of those PAHs varied from 2.9 to 21 mg/kg, on average 11 mg/kg", we can conclude that the samples under test from the 3 Portuguese Tyre Recyclers are well suited for the intended application in "rubber infill".



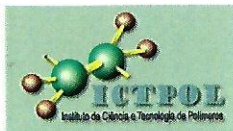
Our laboratory has been measuring PAHs from rubber granulates and has noticed a progressive reduction along the years in the PAHs concentration values, which probably results from the lower content of carbon black and the much smaller presence of old tyres, and subsequently much smaller presence of aromatic oils used as plasticizers.



(Prof. João Carlos M. Bordado)



Substancename	EC No	CAS No.	Blank		Cryoflex® DC-0725 cryogenic rubber infill of RECIPNEU			
			Migration @		Content (sum per group) (mg/kg)	Migration @		Content (sum per group) (mg/kg)
			pH 5.5 (mg/kg)	pH 8.0 (mg/kg)		pH 5.5 (mg/kg)	pH 8.0 (mg/kg)	
Benzo[a]anthracene (BaA)	200-280-6	56-55-3	<0.00075	<0.00075	< 0.1	<0.00075	<0.00075	< 0.5
Chrysene (CHR)	205-923-4	218-01-9	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[a]pyrene (BaP)	200-028-5	50-32-8	<0.00075	<0.00075	< 0.5	<0.00075	<0.00075	< 2.5
Benzo[e]pyrene (BeP)	205-892-7	192-97-2	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[b]fluoranthene (BbFA)	205-911-9	205-99-2	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[j]fluoranthene (BjFA)	205-910-3	205-82-3	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[k]fluoranthene (BkFA)	205-916-6	207-08-9	<0.00075	<0.00075		<0.00075	<0.00075	
Dibenzo[a,h]anthracene (DBAhA)	200-181-8	53-70-3	<0.00075	<0.00075	< 0.1	<0.00075	<0.00075	< 0.5
Sum ofPAHs above			<0.006	<0.006	< 0.7	<0.006	<0.006	< 3.5



			BIORG 0.8-2.5mm of BIOSAFE			G8TA100825 0.8-2.5mm of BIOGOMA		
			Migration @		Content (sum per group)	Migration @		Content (sum per group)
Substancename	EC No	CAS No.	pH 5.5 (mg/kg)	pH 8.0 (mg/kg)	(mg/kg)	pH 5.5 (mg/kg)	pH 8.0 (mg/kg)	(mg/kg)
Benzo[a]anthracene (BaA)	200-280-6	56-55-3	<0.00075	<0.00075	< 0.5	<0.00075	<0.00075	< 0.5
Chrysene (CHR)	205-923-4	218-01-9	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[a]pyrene (BaP)	200-028-5	50-32-8	<0.00075	<0.00075	< 2.5	<0.00075	<0.00075	< 2.5
Benzo[e]pyrene (BeP)	205-892-7	192-97-2	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[b]fluoranthene (BbFA)	205-911-9	205-99-2	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[j]fluoranthene (BjFA)	205-910-3	205-82-3	<0.00075	<0.00075		<0.00075	<0.00075	
Benzo[k]fluoranthene (BkFA)	205-916-6	207-08-9	<0.00075	<0.00075	<0.00075	<0.00075	<0.00075	< 0.5
Dibenzo[a,h]anthracene (DBAhA)	200-181-8	53-70-3	<0.00075	<0.00075	< 0.5	<0.00075	<0.00075	< 0.5
Sum ofPAHs above			<0.006	<0.006	< 3.5	<0.006	<0.006	< 3.5