



Toxicity and mutagenicity of low-metallic automotive brake pad materials



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ABSTRACT

Organic friction materials are standardly used in brakes of small planes, railroad vehicles, trucks and passenger cars. The growing transportation sector requires a better understanding of the negative impact related to the release of potentially hazardous materials into the environment. This includes brakes which can release enormous quantities of wear particulates. This paper addresses *in vitro* detection of toxic and mutagenic potency of one model and two commercially available low-metallic automotive brake pads used in passenger cars sold in the EU market. The model pad made in the laboratory was also subjected to a standardized brake dynamometer test and the generated non-airborne wear particles were also investigated. Qualitative “organic composition” was determined by GC/MS screening of dichloromethane extracts. Acute toxicity and mutagenicity of four investigated sample types were assessed *in vitro* by bioluminescence assay using marine bacteria *Vibrio fischeri* and by two bacterial bioassays i) Ames test on *Salmonella typhimurium* His⁻ and ii) SOS Chromotest using *Escherichia coli* PQ37 strain. Screening of organic composition revealed a high variety of organic compounds present in the initial brake pads and also in the generated non-airborne wear debris. Several detected compounds are classified by IARC as possibly carcinogenic to humans, e. g. benzene derivatives. Acute toxicity bioassay revealed a response of bacterial cells after exposure to all samples used. Phenolic resin and wear debris were found to be acutely toxic; however in term of mutagenicity the response was negative. All non-friction exposed brake pad samples (a model pad and two commercial pad samples) were mutagenic with metabolic activation *in vitro*.

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1. Introduction

Road traffic is known for contributing to the environmental pollution via gaseous and particulate emissions. These emissions were well described for sources such as diesel and gasoline engines emitting organic compounds, elemental carbon and various metal-based compounds (EPA, 2002; Sydbom et al., 2001). Less information was published on chemical composition of non-combustion derived emissions and, particularly, wear of brake pads. According to a report from Ward's Auto 2013, the total number of automobiles worldwide has reached the 1 billion unit mark in 2010, and it is expected that this number will double in

2035. Due to the fact that each automobile produces several mg of wear particles per kilometre, which can be released into the environment (Garg et al., 2000), the total amount of emissions produced cannot be neglected and proper strategies reducing this source of pollution should be designed. Several studies published chemical composition and morphology of wear particles released by braking of passenger cars and focused mainly on the inorganic components such as metal compounds and forms of elemental carbon (Kukutschová et al., 2011; 2010). However, there is a lack of studies dealing with a detailed description of the organic compounds present in the initial brake pad materials (nonsubjected to friction) and in/on wear particles which can be released into the environment in form of suspended and settled fractions (Plachá et al., 2016). Particularly, the released particles may potentially pose some health and environmental risks (Gasser et al., 2009; Rothen-Rutishauser et al., 2008).

A characteristic “organic brake pad” is a multicomponent

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polymer matrix composite typically formulated of more than 10 constituents. The matrix is often a phenolic resin and a quantity of several thousands of different raw materials, typically metals, metal compounds, various minerals, ceramics, polymers and carbonaceous components, that have been used in different brands. The content of metals, especially Fe, may influence the toxicity effect by inducing the oxidative stress (Filip et al., 1997; Malvindi et al., 2014).

The objective of this study was to detect the acute toxicity and mutagenicity of two frequently used, commercially available pads (both containing copper and copper-free that represent the old generation of low-metallic pads and a new formulation reflecting the environmental risks of Cu release into the environment, respectively) and one model brake pad material. In addition, neat phenolic resin- and antimony trisulfide samples were included in the research in order to predict which compounds could be potentially hazardous within multicomponent samples.

2. Experimental

2.1. Tested samples

Four types of samples were used in this study: *i*) two commercial low-metallic automotive brake pads marked as sample I and sample II used for passenger car brakes of some of car manufacturers in the EU, *ii*) a model brake pad with known formulation resembling a typical “low-metallic” friction material, *iii*) brake wear particles (non-airborne wear debris) generated by a simulation of various braking scenarios released from the model brake pad formulation in the standardized A04D brake dynamometer wear test, and *iv*) phenolic resin and antimony trisulfide representing two ‘initial components’ which could potentially contribute to mutagenicity of the brake pad samples, and are frequently used in friction materials formulation.

The commercial samples were kindly provided by their manufacturers. The model friction material was made in the laboratory at Southern Illinois University Carbondale, USA by mixing all ingredients, hot pressing and thermal post-curing, which is very close to the procedure of the manufacturing process. The content of the ingredients is listed in Table 1. Since the performed study addressed the ‘organic’ constituents, the amounts of phenolic resin were intentionally higher (about 15 wt%) in the model pad than typical for after-market brake pads containing the commonly used representatives of abrasives, solid lubricants, reinforcing agents, fillers and a binder.

Total mass of one model brake lining pad is 113 g, and two pads were used in the full-scale brake dynamometer test. The brake pads were manufactured by mixing all ingredients in a Littleford W-10 vertical batch mixer (30 min), moulding, and hot pressing (180 °C/45,000 N/15 min), followed by post curing in air at 180 °C

for 4 h. A Ford Crown Victoria 1999 set-up with the corresponding original equipment, a cast iron disc and calliper, was used in A04D dynamometer test (LINK Engineering M2900).

For further analysis, the two commercial and one model friction composite samples were ball milled for 10 min using a laboratory vibrating mill VM4 (MOBIKO, Czech Republic) with stainless steel beads and subsequently sieved through a 200 µm sieve to receive powder samples. Obviously, the milling process did not generate the same material as friction processes related to the braking, however the testing of the material obtained by milling allowed to estimate the acute toxicity and mutagenicity of the initial material and to estimate changes of these properties before and after the friction process. A sieved fraction of each sample was used for further analyses and it contained a majority of particles with a size varying between 5 and 200 µm, as determined by the particle size distribution measurement (Mastersizer 2000, Malvern Instruments UK).

The non-airborne wear debris sample was collected as the settled fraction by sweeping the surface of the dynamometer chamber after the entire A04D test simulating a mild urban driving. This material can represent the fraction emitted by braking of automobiles, settled on road surfaces and deposited in roadside environments. The individual raw materials (phenolic resin, antimony trisulfide) were used in ‘as received’ state.

2.2. Methods utilized

2.2.1. Organic analysis

Dichloromethane extractions of investigated organic components were performed by a pressurized solvent extraction using a Speed Extractor E-916 (BüchiLabortechnik AG, Switzerland). Five 3.00 ± 0.01 g samples were extracted in dichloromethane (HPLC grade, Sigma Aldrich) in 3 cycles at 110 °C and 100 bars. The crude extracts were placed into a vacuum evaporator and concentrated to a volume of approximately 5 ml under nitrogen flow at 40 °C (Plachá et al., 2016). The resulted extracts were cleaned through a silica gel chromatography column, evaporated to a final volume of 1 ml under nitrogen atmosphere, and immediately analyzed by GC/MS.

GC/MS screening was performed using a quadrupole mass spectrometer (Agilent Technologies MSD5975C) in connection with a gas chromatograph (Agilent Technologies 7890 N) equipped with a capillary column DB-XLB (30 mm × 0.25 mm × 0.25 µm). The GC/MS operating conditions were: the ion source operated in 230 °C, the injection port maintained at 290 °C, and the injection of samples in split less mode followed by 1.5 min purge after the injection.

The program column temperature started at 40 °C for 2 min, then increased by 5 °C/min to 300 °C, and was held for 10 min at 300 °C. The scan mode was employed after an additional, 6-min delay time. The experimental data were measured in the range of 50–550 amu. The obtained data were subsequently evaluated by using the mass-spectra library NIST011, and confirmed by Willey Registry of Mass Spectral Data, 9th Edition. The tentative identifications reflect the most reasonable match in the mass spectral libraries. Only compounds with a high or moderately high confidence in structure were identified. This means an excellent (RSI > 900) or good (RSI=800–900) match between the mass spectrum and that of the electron ionization mass spectra library, where RSI is one of the factors describing the accuracy of that match to the identified spectrum (González-Barreiro et al., 2009).

2.2.2. Analysis of metals

Selected metals were analyzed by the atomic emission spectroscopy with inductively coupled plasma (SPECTRO Vision EOP) after a partial acid decomposition of the solid brake and debris

Table 1
Formulation of the initial model brake-pad composite.

Inorganic constituent	Wt%	Carbon containing constituent	Wt%
Steel fiber	10	Phenolic resin	24
Iron powder	3	Coke	15
Vermiculite	5	Synthetic graphite	5
ZrSiO ₄	2	Resilient graphitic carbon (RGC)	5
BaSO ₄	9	Nitrile rubber (NBR)	5
Copper	4	Twaron	2
MgO	3		
Sb ₂ S ₃	3		
Tin	3		
MoS ₂	1		
Al ₂ O ₃	1		

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