LIPID PEROXIDATION CAUSED BY THE BRAKE WEAR DEBRIS AND CHOSEN CONSTITUENTS OF FRICTION COMPOSITES

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Abstract

Brake processes have been extensively studied and discussed in the relation to the creation of the brake wear. However, the contribution to the environmental pollution is still not clear and there is not unified procedure for the evaluation of the potential risk of the brake wear to the environment and human health. Lipid peroxidation, which could be defined as the oxidative deterioration of lipids containing any number of carbon-carbon double bonds especially polyunsaturated fatty acids, is one of the markers of oxidative stress and linoleic acid as a model lipid of cell membrane is used to quantifying the potency of tested compounds to induce peroxidation damage (lipoperoxidation) of unsaturated lipids.

The aim of the study is evaluation of the potential toxicity of brake wear debris and typical constituents used in formulation of friction composites for brake linings by cell-free chemical test. For quantifying of lipoperoxidation was used test based on the reaction of malondialdehyde (natural product of lipid peroxidation) with thiobarbituric acid to produces pink adduct. Brake wear debris from commercial available brake pads and reference friction composites were collected after standard brake dynamometer test. Lipoperoxidation was evaluated for the collected brake wear debris and for chosen compounds commonly used in brake formulations (titanate, barite, iron fibers, bronze fibers, and chromite). Both types of brake wear debris were analyzed by scanning electron microscopy and Raman spectroscopy. Experimental results showed slightly toxic character for chromite, iron fibers, barite, and brake wear from reference friction composite.

Keywords: Lipid peroxidation, brake wear debris, oxidative stress, friction composites, environmental pollution

1. INTRODUCTION

Brake wear debris is important source of emissions originated from road traffic and may pose negative impact to the living organisms [1]. Friction composite for brake lining is heterogeneous mixture of different components providing optimal technical parameters for breaking, generally consists of more than 10 constituents including fiber reinforcements, abrasives, lubricants, fillers, and phenolic binders [2]. Braking is friction process connected with high temperature and pressure during which wear debris is produced, partially with different composition (new often oxidized forms) [3].

In studies on cell systems focused on toxic effect of wear brake debris cytotoxic ability was demonstrated where debris was able to induce oxidative stress and inflammation response of tissue (cells) generally. Several studies found that brake wear particles cause damage of tight junctions probably through oxidative stress [4], due to their increased surface and high reactivity with biomolecules [5]. Toxic effect was studied also in several non-cellular systems as lipid peroxidation of polyunsaturated fatty acid, reactive oxygen species generation with 2´,7´-dichlorodihydrofluorescein dye [1], or electron paramagnetic resonance [7]. Non-cellular systems have several advantages: small sample consumption, well defined system without interferences, and low-culture conditions. The disadvantage is the scope of the method where only one metabolic pathway without connection to other is monitored. Non-cellular tests therefore seem appropriate for the initial evaluation of the potential toxic effects of the studied systems. Method useful for quantifying of toxic effect is lipid peroxidation assay which use polyunsaturated fatty acid as model of cell membrane lipid [7].

The aim of the study was to perform basic characterization of collected brake wear debris after standard dynamometer test and selected typical constituents used in formulation of friction composites for brake linings and evaluation of the potential toxicity by cell-free chemical test of lipid peroxidation. Samples were characterized by scanning electron microscope with energy dispersive X-ray spectroscopy SEM/EDX and Raman microspectroscopy to determine morphology and phase composition, respectively.

2. MATERIALS AND METHODS

2.1. Materials

For performance of the ability to induce lipid peroxidation following materials were used: linoleic acid, TiO_2 21 nm (Sigma-Aldrich, Germany), trichloroacetic acid, hydrochlorid acid, butanol (Lachner, Czech Republic), ethanol (Penta, Czech Republic), butylhydroxyltoluene, thiobarbituric acid (Applichem, Germany), $NaH_2PO_4.2H_2O$, $Na_2HPO_4.12H_2O$ (Lachema, Czech Republic), and distilled water.

For determination of ability to induce lipid peroxidation these samples were selected: barite, hexagonal potassium titanate, bronze fibers, iron fibers, and iron chromite which are industrially produced materials commercially used for the production of brake pads and generated brake wear debris (please see chapter 2.2.)

2.2. Brake wear debris generation

For generation of brake wear debris automotive full scale brake dynamometer model M2800 (LINK Engineering) was used. Brake wear debris was collected after standard dynamometer tests. The nonairborne particles (NAP) were collected from surface of dynamometer chamber, the airborne (AP) fraction was collected from filter (KS 85 Klima - Service, a.s., Czech Republic) located in dynamometer ventilation system. The AP contains particles from different low metallic brake pads and more simulate real traffic conditions. The non-airborne NAP-1 sample originated from reference brake pad (BP-1). Formulation of BP-1: bronze, brass, CuS, Sn, Fe fibers, coke, graphite, aramid fibers, $FeCr_2O_4$, $BaSO_4$, ZrO_2, SiO_2, SiC, Al_2O_3, MgO, MoS_2, ZnO, rubber, SnS, and phenolic resin. The non-airborne NAP-2 sample originated from brake pad (BP-2) which has the same composition as reference brake pad with addition of 10% hexagonal potassium titanate (formulation of this brake pad was the same as in the case of BP-1 and all weights of used components were proportionally decreased to obtain same amount of the composite with potassium titanate).

2.3. Analytical methods used for characterization of tested materials

Experimental data on morphology and elemental composition of studied materials were obtained from scanning electron microscope (SEM) (Philips XL-30), equipped with EDX (EDAX) analysis, samples were attached on the carbon conductive tape. Smart Raman system XploRA™ (HORIBA Jobin Yvon) with laser 532 nm (10% of initial laser signal), and grating 1200 grooves/mm was used for measurements of generated brake wear particles. Absorbance of lipid peroxidation assay was evaluated by UV/VIS spectrometer CINTRA 303 (GBC Scientific Equipment).

2.4. Lipid peroxidation

The assay used for quantifying of lipoperoxidation is based on the reaction of malondialdehyde (end product of lipid peroxidation) with thiobarbituric acid to produces pink product that absorbs at 532 nm. 9 mg of tested materials were suspended in 3ml of a buffered (sodium phosphate buffer 0.01M, pH 7.4) micellar dispersion of linoleic acid (0.001M) containing 2.5 wt.% of ethanol. The suspension was stirred under indoor UV illumination (REPTI GLO 5.0, 26W) at 37 °C for 72 h. The tested material was removed by centrifugation (12000 rpm, 30 min) with ethanol solution of butylhydroxytoluene (0.2 wt.%). 1 ml of resulting solution was mixed with 2 ml of thiobarbituric acid (0.034M) solution containing HCl (0.025 M), and trichloroacetic acid (0.92M) and heated in a boiling water bath for 30 min. Final pink complex was extracted to 3 ml of 1-

butanolafter cooling in an ice bath. Absorbance of the organic phase was measured at 532 nm by UV/VIS spectrometer. The whole experiment was three times repeated. The assay used in the study was modification of study presented by Corazzari et al. [7].

3. RESULTS AND DISCUSION

Morphology (**Figure 1**) and elemental composition (**Table 1**) of commercially utilized materials used for preparation of tested friction composites (NAP-1 and NAP-2) were characterized by SEM/EDX.

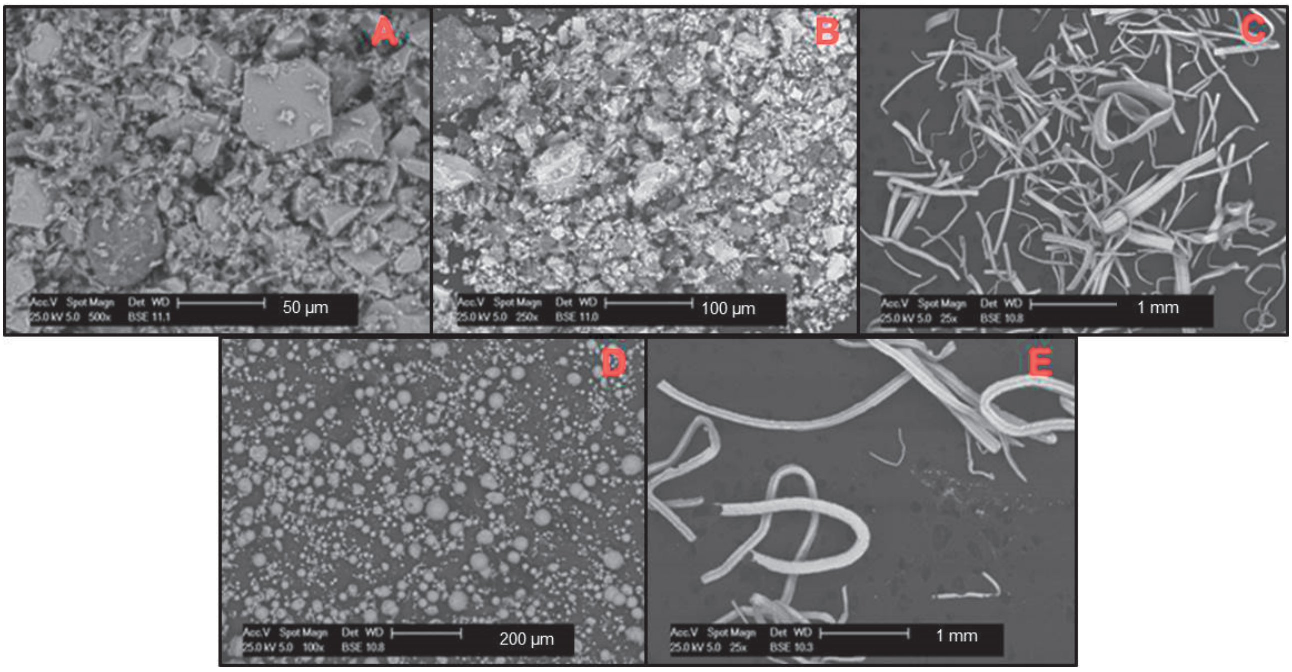

Figure 1 SEM images of (A) iron chromite, (B) barite, (C) iron fibers, (D) hexagonal potassium titanate, and (E) bronze fibers

Table 1 Summary of elements detected by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) in the studied raw materials

Material	SEM/EDX
Iron chromite	Fe, Cr, O
Barite	C, O, S, Ba, Mg, Ca, Fe
Iron fibers	Fe
Hexagonal potassium titanate	O, K, Ti
Bronze fibers	O, Cu, Sn

Detected elements in these samples show that commercially used materials are without impurities, except barite. Barite contains additive of magnesium, calcium, iron, and carbon. **Figure 1** shows different shapes and sizes of particles, which correspond to the different function of these materials in brake formulations. Barite and titanate are used as fillers, copper alloys and iron fibers as reinforcements, and chromite as abrasive [8]. These materials were selected, because they were used in our reference friction composites, as well they are typical representatives of brake composites, and are relatively highly represented in formulation of friction composites.

Figure 2 displays selected images from SEM analysis which showed different morphology, size, and shape of studied wear particles. In all cases samples have heterogeneic nature. Image AP in **Figure 2** represents airborne particles, which are in comparison to non airborne particles (NAP-1, NAP-2) several times smaller but as well the sample contains larger particles about 100 - 200 μm in diameter. NAP-1 showed complex and heterogeneous mixture of particles with different size and shape, which includes spherical, plated, sharp edged, and fibre particles. Spherical particles are typicaly created during high-temperature processes [9]. NAP-2 in comparison to NAP-1 contains bigger amount of sharp edged particles, which origin is connected with mechanical wear.

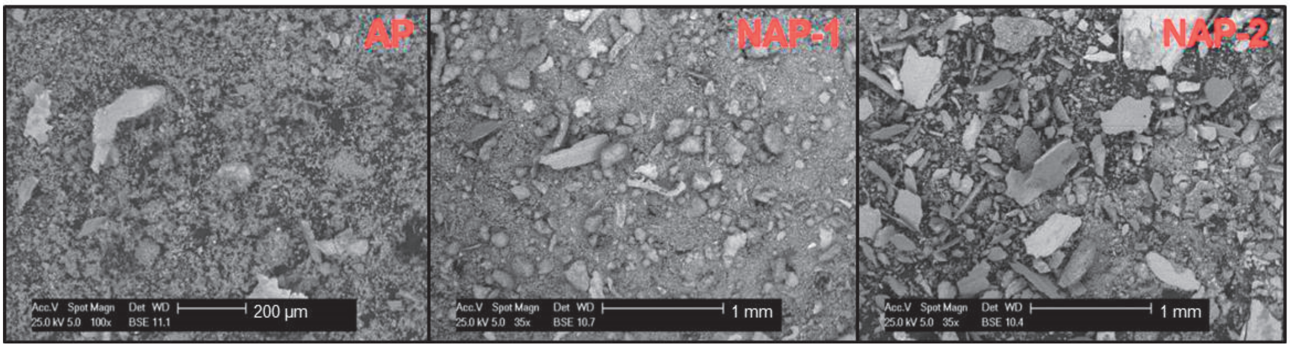

Figure 2 SEM images of airborne particles from pocket filter (AP), non-airborne particles from referent friction composite (NAP-1), non-airborne particles from friction composite with addition of titanate (NAP-2)

Table 2 summarizes elemental composition of wear debris particles evaluated by SEM/EDX and phase analysis (detected compounds) by Raman microspectroscopy. Composition of the NAP-1 and NAP-2 samples corresponds to the used raw materials in brake pad formulations (see chapter 2.2). Difference between NAP-1 and NAP-2 is caused by addition of hexagonal potassium titanate in friction composite. Presence of Ca, which was not used in the initial formulation in the NAP-2 sample is probably due to the impurity of the barite (see **Table 1**). AP sample was obtained from more than 10 different low-metallic brake pads, but from the results (see **Table 2**) it is evident, that detected elements and compounds correlate with NAP-1 and NAP 2 samples. Raman microspectroscopy determined amorphous carbon as main compound in the all studied samples, which is probably caused by the phenolic resin degradation [10].

Table 2 Summary of the detected elements by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) and compounds by Raman microspectroscopy

Material	SEM/EDX	Raman microspectroscopy
AP	C, O, Fe, Cu, Si, S, Zn, Ba, Cr, Mg, Ti, Al, Sn	amorphous carbon, graphite, silicates, Cu_2O, MoS_2, Fe_2O_3, Fe_3O_4
NAP-1	C, O, Fe, Cu, Si, S, Zn, Ba	amorphous carbon, graphite, MoS_2, Fe_2O_3, Fe_3O_4, chromite
NAP-2	C, O, Fe, Cu, Si, S, Zn, Ba, Cr, Mg, Ti, Ca, K	amorphous carbon, graphite, Fe_2O_3, Fe_3O_4, chromite, pottasium titanate

Break wear particles may differ considerably from the bulk friction material [2], for example iron oxides were detected, but only iron powder was used in formulation of composite. During braking high temperatures and pressures are applied which may lead to the formation of the new products (for example oxidation of metallic component mainly cooper and iron) [3]. Difference in composition detected by SEM/EDX and Raman microspectroscopy may be caused by tendency of wear to form aggregates, where different particles can cover homogenous core, layer of amorphous carbon on particles surface or interference of carbon conductive tape.

Ability to induce oxidative stress via peroxidation of polyunsaturated fatty acid, linoleic acid exactly was evaluated for all studied samples (**Figure 3**).

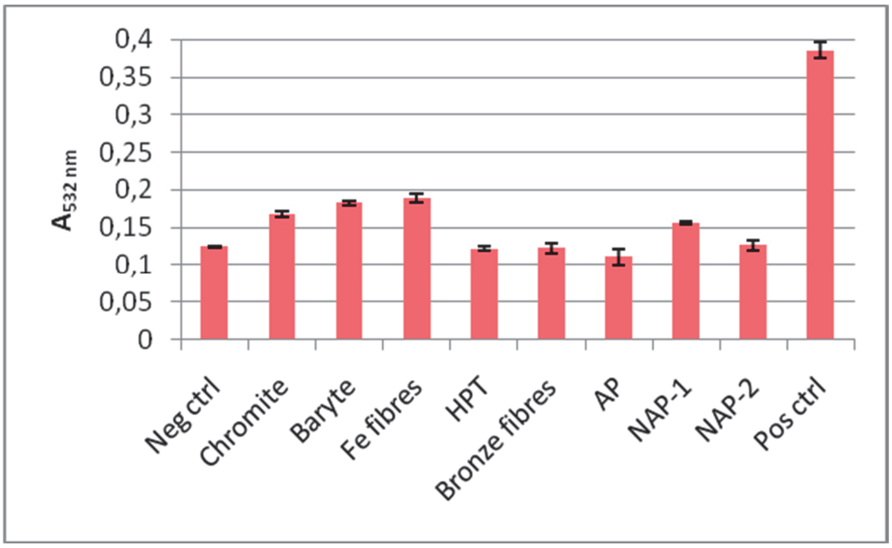

Figure 3 Absorbance (532 nm) of pink complex malondialdehyde - thiobarbituric acid corresponds to level of lipoperoxidation of linoleic acid incubated with analyzed materials for 72 h at 37 °C with UV illumination. HTP-hexagonal potassium titanate, AP-airborne particles, NP-1-non-airborne particles from referent brake composite, NP-2-nonairborne particles from brake composite with addition of titanate, negative control (ctrl) - linoleic acid, positive control (ctrl) - TiO_2. Data are reported as mean ± SD of three measurements

Significant increase of lipoperoxidation ability from materials forming brake composite shows chromite, barite, and iron fibers. Chromium enters cells poorly, but can bind to DNA and induces mutagenesis. Barite is very poorly absorbed in the organism and its inhalation may cause benign pneumoconiosis, and in cell membranes can block the K^+ channels in Na-K pump. Iron can cause oxidative stress, because catalyzes the formation of radical, which can damage tissues and biological molecules [11]. Titanate and bronze fibers oxidized linoleic acid equally as nonspecific oxidative processes, which are not active in oxidizing linoleic acid.

Airborne particles are generally considered to be more toxic than non-airborne particles. It is caused by their higher reactivity depend on larger surface of particles [10]. Airborne particles may permeate into lung and can be transported to the whole organism. They were not able to induce lipoperoxidation in used test. It can be caused by aggregating of particles in bigger structures. From NAP samples only NAP-1 is active in oxidizing of linoleic acid. Higher values in case of iron fibers can by caused by presence of iron oxides, detected by Raman. Decrease of value in NAP-2 in comparison to NAP-1 is probably caused by addition of 10% titanate, which does not cause lipid peroxidation (see **Figure 3**). Probably toxicity of brake wear debris is the most influenced by coating of these particles by amorphous carbon [5], which was detected in majority and as well by presence of metal oxides (especially iron oxides) in the sample.

4. CONCLUSION

Morphology, elemental, and phase composition of selected raw materials used in brake pad formulation (chromite, barite, iron fibers, titanate, and bronze fibers) and wear particles produced from braking process (airborne and non-airborne fraction) were identified by SEM/EDX and Raman microspectroscopy. Analysis showed that all input materials except barite are pure and composition of wear particles of NAP-1 and NAP-2 samples corresponds to initial formulation of brake composites. Sample AP, however, it is mixture of wear of 10 different brake pads have very similar composition to NAP samples. In all cases wear particles have heterogeneous character and airborne particles are several times smaller in diameter than non-airborne.

Evaluation of ability of tested materials to induce oxidative stress via lipid peroxidation showed that only chromite, barite, iron fibers, and NAP-1 sample are able to induce lipoperoxidation in used test.

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