

AQUATIC TOXICITY ASSESSMENT OF THE AIRBORNE BRAKE WEAR DEBRIS AND BINDERS OF FRICTION COMPOSITES (PHENOLIC RESINS)

PEIKERTO VÁ Pavlína^{1,2}, ČABANOVÁ Kristina¹, VACULÍK Miroslav¹, KUČOVÁ Karla¹

¹ VSB - Technical University of Ostrava, Nanotechnology Centre, Ostrava, Czech Republic, EU

² VSB - Technical University of Ostrava, IT4Innovations, Ostrava, Czech Republic, EU

pavlina.peikertova@vsb.cz

Abstract

Pollution associated to road traffic and its combustion processes are considerably discussed in recent years. Nowadays, attention is also paid to the non-combustion processes, such as braking. During braking nonairborne and airborne fraction is released into the environment. Manufacturers try to use materials with low environmental risks, but during braking new compounds can be created, due to the high temperatures and pressures. Both fractions as well contain considerable amounts of nano-sized particles which may consequently enter the water environment and may pose risk to the living organisms. However, there are no standardized and unified procedures which could be used for the brake wear debris toxicity assessment.

Aim of the study was the evaluation of the acute aquatic toxicity of the airborne brake wear debris and the most commonly used binders (phenolic resins) in the friction composites for brake linings. Brake wear debris from low-metallic brake pads was collected after standard dynamometer test from pocket filter and characterized by Raman microspectroscopy and scanning electron microscopy. Phenolic resin as binder is material with the highest volume in the formulation of the friction composite and contains Hexamethylenetetramine (HMTA) which can be decomposed at the ammonia and formaldehyde in high temperatures. Three commercially available phenolic resins were tested in the initial state and as well after thermal treatment (160 °C), which simulate process of manufacturing. Scanning electron microscopy and Fourier-transform infrared spectroscopy were used for characterization of phenolic resins. EC₅₀ toxicity parameter for freshwater green algae detection organism *Raphidocelis subcapitata* was evaluated for all tested materials.

Keywords: Acute aquatic toxicity, airborne brake wear debris, friction composite, phenolic resin, *Raphidocelis subcapitata*

1. INTRODUCTION

Friction materials that are used in automotive brake pads formulation are complex mixtures [1]. Recently, environmental requirements for new brake and disc materials are becoming increasingly important due to the increasing contribution of non-combustion emissions to traffic pollution [2, 3]. Nowadays, there is paid more attention to the friction processes connected with the braking, due to the fact that friction composites are very heterogeneous and contain several possible harmful materials, e.g. copper [4]. More importantly, however, there are newly formed particulates with a different chemistry, when compared to the original bulk materials, released during the friction processes, accompanied with complex physico-chemical interactions on the surfaces [5]. Therefore, there is no unified methodology for the study of the environmental and health impact of the brake wear debris, but there are published reviews, which summarize the recent research in this field [6, 7]. Published studies suggest that brake wear debris has a potential environmental risk.

Aim of the study was evaluation of the acute aquatic toxicity parameter EC₅₀ for freshwater green algae *Raphidocelis subcapitata*. The parameter was determined for the airborne brake wear debris collected after standard dynamometer procedures. The airborne fraction was chosen to its higher environmental risk, because contains very small particles mainly nano-sized particles. Then were chosen the most commonly used binders

(phenolic resins) in its initial state and after thermal treatment (160 °C) and its main constituent hexamethylenetetramine were also tested by aquatic toxicity assessment. All materials were characterized by Raman microspectroscopy, Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to determine their composition and morphology.

2. MATERIALS AND METHODS

2.1. Materials

Three commercially available phenolic resins denoted as PR1, PR2, and PR3, were characterized and tested by toxicity assessment. Phenolic resin is a commonly used binder in brake pads formulation in relatively high amounts. Samples of phenolic resins were also tested after thermal treatment at 160 °C, which simulate process of manufacturing of brake pads. Main constituent of the resin, hexamethylenetetramine (HMTA) and as well the sample of airborne brake wear debris from ten different low steel commercially available brake pad were also tested and characterized.

2.2. Friction testing and brake wear debris generation

Automotive full scale brake dynamometer model M2800 (Link Engineering) and the standard dynamometer tests AKM-SAE J2522 and ISO 26867) were used for generating the airborne brake wear debris (BWD). The airborne fraction was collected from filter (KS 85 Klima - Service, a.s., Czech Republic) standardly located in the brake dynamometer ventilation system. BWD sample contains particles from ten different commercially available low metallic brake pads. This mixture probably better represents real situation on the European roads, but unfortunately there is no available information about the initial brake pads formulation.

2.3. Methods of characterization

Mid-IR spectra were obtained for samples in solid original state by a Fourier transform infrared spectrometer Nicolet 6700 (Thermo Scientific), using the single reflection ATR technique on a diamond crystal. Measurements were performed with a resolution of 4 cm⁻¹ and 32 scans.

BWD sample was characterized by Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France). Raman spectra were acquired with 532 nm (20 - 25 mW) excitation laser source, and 1200 grooves/mm grating in the range 100 - 4000 cm⁻¹. The intensity of the laser beam was changed based on the sample signal from 1 to 10% of initial laser beam. Spectra were compared with coupled Raman spectral library.

Scanning electron microscope with energy dispersive spectrometer (Philips XL30 with EDX analysis APOLLO X (EDAX)) was used for the morphology characterization and determination of the elemental composition.

2.4. Aquatic toxicity assessment

Aquatic toxicity assessment was evaluated by using green algae *Raphidocelis subcapitata*, which is commonly used as a bioindicator species to assess the levels of nutrients or toxic substances in freshwater environment. The leachates were prepared in accordance with European technical standard EN 12457-2 [8]. Samples were leached in deionized water in continuous rotation container for 24 h. After mixing for 24 h the mixture was filtered through a nitrocellulose membrane filter (Pragopor, Pragochema s.r.o.) with an average pore size of 0.45 µm.

The toxicity assessment was performed in accordance with the OECD 201 methodology, i.e. monitoring the growth inhibition of organisms (*Raphidocelis subcapitata*) after 72-h exposure to the tested material [9]. For the evaluation of the parameter EC₅₀ were created concentration series and the highest concentration was chosen to compile solid to liquid ration 1:10 according to the European standard EN 12457-2 [8].

Data obtained for exposed samples were compared with the control samples and are given as percentage of algae growth inhibition or stimulation. To determine the acute aquatic toxicity of the aqueous leachates of the studied samples it was necessary to adjust pH value to be within the physiological range of 8.1 ± 0.2 for the given species. The concentration series and control samples were inoculated with the same volume of the algae suspension to achieve the cell concentration of 10,000 cells per cm^3 . Thus the prepared test samples were cultivated ensuring constant temperature and light conditions for 72 h. Algal cell density was measured by using Olympus CX31 light microscope and Bürker counting chamber.

3. RESULTS AND DISCUSSION

Morphologies of the studied samples are shown in **Figure 1**. It is evident that sample PR2 contains a little bit smaller particle in the comparison of the sample PR1 and PR3. Particles detected in the sample of HMTA are approximately 5 times bigger than in case of the samples PR1 - PR3. On the contrary morphology of the BWD sample (**Figure 1**) shows very heterogeneous mixture of spherical and sharp edged particles, which correspond to the different source of origin thermal and abrasive wear, respectively. **Table 1** summarizes detected elements in the BWD sample and chosen EDX pattern of the BWD sample is shown in **Figure 1**. Detected elements in remain samples corresponding to their structure and so are not listed.

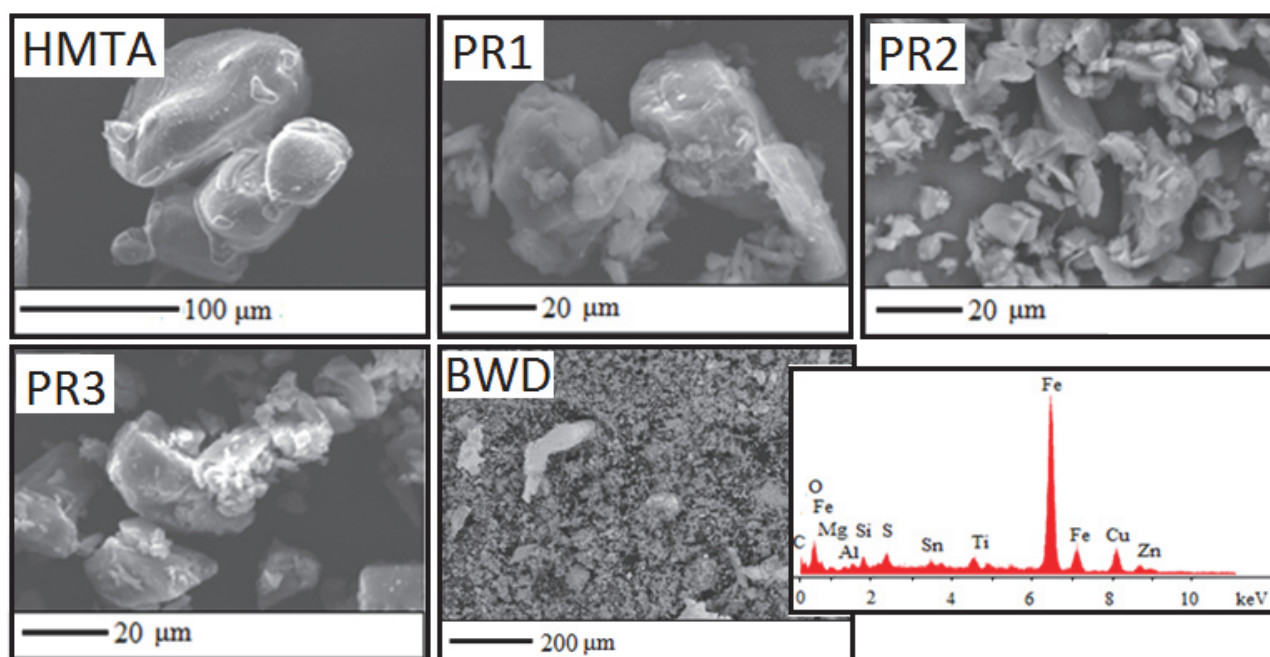


Figure 1 Scanning electron microscopy (SEM) images of studied samples HMTA (hexamethylenetetramine), PR1 (phenolic resin 1), PR2 (phenolic resin 2), PR3 (phenolic resin 3), and BWD (brake wear debris) with corresponding energy dispersive X-ray spectroscopy pattern (EDX) of BWD

Measured infrared spectra of HMTA and PR1 - PR3 samples are shown in **Figure 2**. Spectra contain bands which represent typical vibrations of these compounds. Main HMTA bands are presented below 3000 cm^{-1} (C-H stretching symmetric and asymmetric vibrations) and at 1452 , 1360 , and 1230 cm^{-1} (assigned respectively to asymmetric $-\text{CH}_2$, symmetric $-\text{CH}_2$, and stretching C-N vibrations) [10]. Spectra of PR1 and PR3 samples contain as well these HMTA bands and, therefore, confirm HMTA as main component of phenolic resin. All three samples of phenolic resin are very similar to each other, thus no significant differences in their structure are expected. In the case of sample PR3 there is very intense broad band at $\sim 3300 \text{ cm}^{-1}$, which corresponds to the O-H vibrations and its higher intensity can be caused by more humidity in the sample.

Table 1 Detected elements by scanning electron microscopy coupled with energy dispersive X-ray spectroscopy SEM-EDX and compounds by Raman microspectroscopy in brake wear debris sample

SEM-EDX	Raman microspectroscopy
Al, Ba, C, Cr, Cu, Fe, Mg, O, S, Si, Sn, Ti, Zn	Amorphous carbon, graphite, silicate, Cu ₂ O, MoS ₂ , Fe ₂ O ₃ , Fe ₃ O ₄

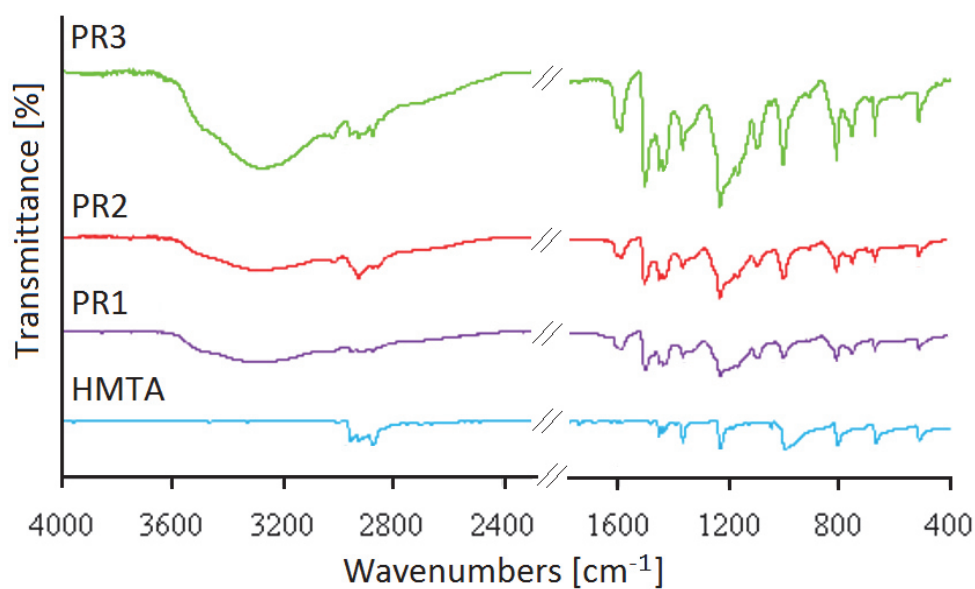


Figure 2 Measured FTIR (Fourier-transform infrared spectroscopy) spectra of HMTA (hexamethylenetetramine), PR1 (phenolic resin 1), PR2 (phenolic resin 2), and PR3 (phenolic resin 3) samples

Due to the limited space of the paper FTIR spectra of thermally treated phenolic resins PR1_T - PR3_T are not shown. However, all bands which were detected in untreated samples were also detected in these samples, but these bands were broader which suggest to the more amorphous character of the thermally treated samples. As well the broad bands at $\sim 3300\text{ cm}^{-1}$ were less intensive, which may correspond to the decrease of humidity in the sample. No significant changes in the structure were observed, because degradation of the phenolic resin is expected at higher temperatures above $200\text{ }^{\circ}\text{C}$ [11] and the $160\text{ }^{\circ}\text{C}$ is sufficient temperature for cross linking and binding all components in the friction composite [12].

Determined phase composition of the BWD sample by Raman microspectroscopy is shown in **Table 1**. Compounds were determined by comparison with Raman spectral library. There is no information about initial composition of the samples, due to the know-how of brake manufacturers, but the detected compounds and elements (**Table 1**) correspond to the generally used compounds in brake formulations. FTIR measurements (spectra not shown in the paper) revealed very little information about sample composition, so Raman microspectroscopy was used for the sample characterization. Raman measurements proved very high amount of amorphous carbon, which absorbance is very high, so FTIR method is not suitable for this type of sample.

Evaluated toxicity parameters (EC_{50}) for all studied samples are shown in **Figure 3**. The most toxic sample was determined the HMTA sample. It could be caused by HMTA highly solubility and our results are in good agreement with the safety data information. Toxicity parameters for untreated PR samples have different values which vary from 3.7 to 7.7. However, similar trend was observed for the thermally treated samples, where all these samples have higher toxicity parameter, thus they are less toxic. So, temperature $160\text{ }^{\circ}\text{C}$, which is not so high as decomposition temperature, leads to the cross linking of the phenolic resin structure

and decreases the toxicity effect of the phenolic resins. Last but not least was determined the toxicity parameter for the collected airborne brake wear debris, which value is relatively very high. But there is need further study to determine the possible influence of the accumulation and long term exposition of these particles.

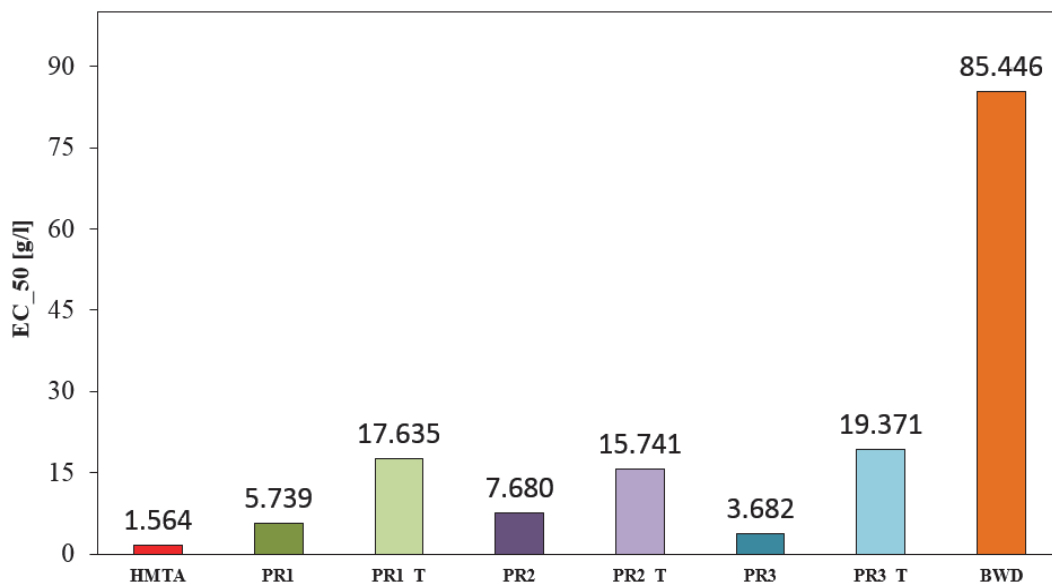


Figure 3 Evaluated EC₅₀ parameter for all tested materials. HMTA (hexamethylenetetramine), PR1 (phenolic resin 1), PR1_T (thermally treated phenolic resin 1), PR2 (phenolic resin 2), PR2_T (thermally treated phenolic resin 2), PR3 (phenolic resin 3), PR3_T (thermally treated phenolic resin 3), BWD (brake wear debris)

4. CONCLUSIONS

All studied samples were characterized by FTIR spectroscopy; however, the FTIR spectrum of BWD shows a little information about its composition. Thus the Raman microspectroscopy was used for the determination of the phase composition of the sample. It was confirmed that BWD is very heterogeneous and contains possibly harmful particles, as copper based compounds. Results from evaluation of the toxicity parameter EC₅₀ show that the most toxic compound was HMTA. Toxicity of the phenolic resins after thermal treatment decreased in all cases. EC₅₀ parameter was for BWD sample relatively very high. However, long term exposure to the BWD and their accumulation in the environment and may have more toxic character for the living organisms.

ACKNOWLEDGEMENTS

This research has been funded by the NPU II - IT4Innovations excellence in science (project no. LQ1602) and the Ministry of Education, Youth and Sports of the Czech Republic (project no. SP2016/78).

REFERENCES

- [1] FILIP, P., KOVARIK, L., WRIGHT, M. Automotive brake lining characterization, *SAE Technical Paper* 973024, 1997, doi:10.4271/973024.
- [2] DENIER VAN DER GON, H.A.C., GERLOFS-NIJLAND, M.E., GEHRIG, R., GUSTAFSSON, M., JANSSEN, N., HARRISON, R.M., HULSKOTTE, J., JOHANSSON, C., JOZWICKA, M., KEUKEN, M., KRIJGSHELD, K., NTZIACHRISTOS, L., RIEDIKER, M., CASSEE, F.R. The policy relevance of wear emissions from road transport, now and in the future-an international workshop report and consensus statement. *Journal of the Air & Waste Management Association*, 2013, vol. 63, no. 2 pp. 136 - 149;

- [3] AMATO, F., CASSEE, F.R., DENIER VAN DER GON, H., GEHRIG, R., GUSTAFSSON, M., HAFNER, W., HARRISON, R., JOZWICKA, M., KELLY, F., MORENO, T., PREVOT, A.S.H., SCHAAP, M., SUNYER, J., QUEROL, X. Urban air quality: the challenge of traffic nonexhaust emissions. *Journal of Hazardous Materials*, 2014, vol. 275, pp. 31-36.
- [4] STRAFFELINI, G., CIUDIN, R., CIOTTI, A., GIALANELLA, S. Present knowledge and perspectives on the role of copper in brake materials and related environmental issues: A critical assessment. *Environmental Pollution*, 2015, vol. 207, pp. 211-219.
- [5] KUKUTSCHOVÁ, J., MORAVEC, P., TOMÁŠEK, V., MATĚJKA V., SMOLÍK, J., SCHWARZ, J., SEIDLEROVÁ, J., ŠAFÁŘOVÁ, K., FILIP, P. On airborne nano/micro-sized wear particles released from low-metallic automotive brakes. *Environmental Pollution*, 2011, vol. 159, no. 4, pp. 998-1006.
- [6] PEIKERTOVÁ, P., FILIP, P. Influence of the automotive brake wear debris on the environment - a review of recent research. *SAE International Journal of Materials and Manufacturing*, 2016, vol. 9, no. 1, pp. 133-146.
- [7] GRIGORATOS, T., MARTINI, G. Brake wear particle emissions: a review. *Environmental Science and Pollution Research*, 2015, vol. 22, no. 4, pp. 2491-2504.
- [8] EUROPEAN STANDARD EN 12457-4:2002: Characterization of waste - Leaching - Compliance test for leaching of granular waste materials and sludges - Part 4: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction), 2002.
- [9] OECD Guideline for Testing of Chemicals, Test No. 201, Alga, Growth Inhibition Test. OECD Publishing; 1984.
- [10] AGWARA, M.O., NDIFON, P.T. NDIKONTAR, M.K. Physicochemical studies of some hexamethylenetetramine metal(II) complexes. *Bulletin of the Chemical Society of Ethiopia*, 2004, vol. 18, no. 2, pp. 143-148.
- [11] *Material safety data sheet - Hexamethylenetetramine*, [online]. 2015 [Cit. 2016-10-01] available from: <http://www.dogee.org/lab/chemicals/1013.pdf>
- [12] SHALIN, R.E. *Polymer Matrix Composites*. Springer Science & Business Media, 1995, ISBN 978-94-011-0515-6.