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## **PHENOLIC RESINS EMISSIONS UPON THERMAL DEGRADATION**

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KEYWORDS – phenolic resins, pollution, brake pads, NH<sub>3</sub>, CO<sub>2</sub>.

### **ABSTRACT**

Consumable materials pollution has been increasing during recent years. The optimization of vehicle engines lead to an important decrease of fine dust related to combustion. On the other hand fine dust, coming from brake pads, pneumatics and roads has been growing. Most of the fine dust produced by consumables is released in urban areas, making its analysis and monitoring an important issue.

A significant part of this kind of pollution is generated by the braking system. In fact almost every terrestrial transport method (cars, bikes, trains or planes) has a braking system. The consumable part of the system is composed by a pad of friction material and a metallic rotor. These pads are composed by a series of ceramic and metallic materials joint together by a polymer matrix, generally a phenolic resin.

The aim of this work is to determine the most significant gases that are released during the thermal degradation of phenolic resins. Thermo-gravimetric analysis (TGA) were carried out using an equipment coupled with mass spectrometer (MS). Two different samples of phenolic resin, commonly used in braking industry, named Phe\_1 and Phe\_2, have been investigated. Thermal degradation has been studied both in air and in inert atmosphere (Argon).

### **INTRODUCTION**

Transportation method emissions are continuously under study in these last decades, because there are many standards (known as EURO norm, for Europe, or tiers, for US) that imposes pollution emissions to decrease. During the last years the major part of the study about transport pollution reduction was concentrated on the engine waste gas that represents the greatest part of the emissions.

Recently, the interest has been also focused on other devices, present in every motorized means of transportation, that produce dust and polluting gases. They are the consumable materials, such as the tire and the braking devices (particularly brake pads and disk).

The degradation of these materials, that, when they are in use, is principally tribological and thermal, produces in fact small particle size dust and dangerous gases [1] that have to be reduced, in order to reduce the environmental impact of transportation.

Concerning the braking pads, they have already been object of normative for the elimination of asbestos and the abatement of copper. Moreover the braking pads industry uses a very large quantity of phenolic resins, for its good property about wear resistance and friction coefficient [2, 3]. Every year hundreds of million brake pads in Europe are produced. Considering an average weight of 150 grams of friction material for brake pad and a percentage of 7% in weight of phenolic resin in each formulation, for a total amount of 1575 ton of resin used approximately per year.

This number increases by an order of magnitude, if the global scale is considered, where there are over a billion of cars. As a consequence, even the small quantities of polluting gas produced by a single pad are likely to represent an environmental issue.

So, the aim of this work is to determine what gases are emitted when phenolic resins thermally degrade, and also to characterize the residual char when decomposition occurs in absence of oxygen. For our tests, we analyzed two phenolic resins commonly used in the braking pads industry, kindly provided in powder form, named hereafter as Phe1 and Phe2. We carried out thermo-gravimetric analysis (TGA) coupled with mass spectroscopy (MS) to reveal which gases are released during the resins thermal degradation.

## EXPERIMENTAL

Thermogravimetric analysis (TGA) were carried out using an equipment (Mettler Toledo TGA1600) coupled with mass spectrometer (MS) (Balzers Quadstar 422). For the measurement, the powder was inserted into an alumina crucible. For the identification of emitted gases, the fragment reported in Table 1 have been considered.

Table 1: Fragments analysed for mass spectroscopy

Gas	MS Fragment [uma/e]
CO <sub>2</sub>	44
NH <sub>3</sub>	17
Alcohols	46
Benzene	78
Phenols	91
Toluene	92

Analysis have been performed both in air and in inert atmosphere (Argon). The heating ramp was 10°C/min, from 25°C to 800°C (the braking pads maximum operating temperature, in the worst condition).

After analysis in Argon, the residual char in the crucible was collected and characterized by Field Emission Scanning Electron Microscopy (FESEM), with a Zeiss Merlin instrument, in order to gain information on the particle size and morphology.

## RESULTS

### TGA-MS in air

Figure 1 shows the TGA curves (percentage by mass versus temperature) of Phe1 and Phe2. Thermal degradation of the two materials is similar, with a significant weight loss at 550°C for Phe1 and at 570°C for Phe2. A difference can be observed in the slope of the two curves, indicating that degradation of Phe2 is apparently slower than for Phe1.

Both curves approach zero at the end of the test, revealing that the samples were completely burnt during the measurement. Indeed, no residual powder was present in the crucible at the end of the measurement

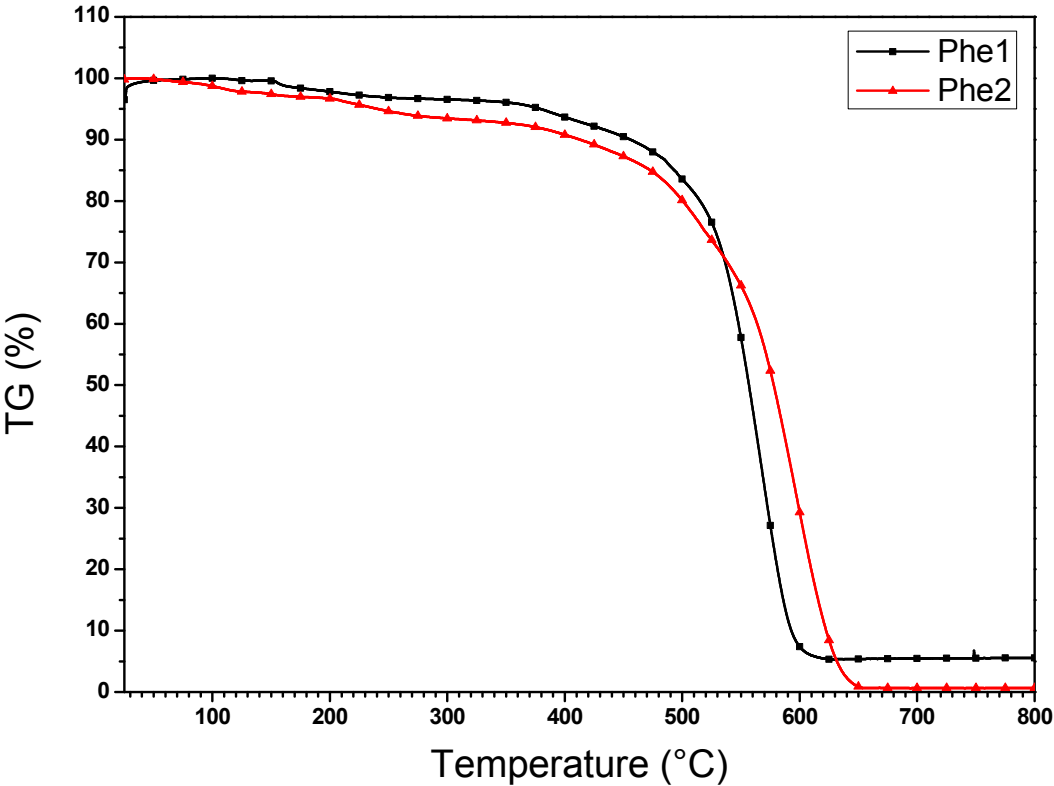


Figure 1: TGA curves of sample Phe1 (black) and Phe2 (red) in air

Figure 2 reports the MS signals related to CO<sub>2</sub> and NH<sub>3</sub>. These gases are known to be generated by the decomposition of phenolic resins [4]. In agreement with the similar TGA curves, no significant differences are observed between the two samples.

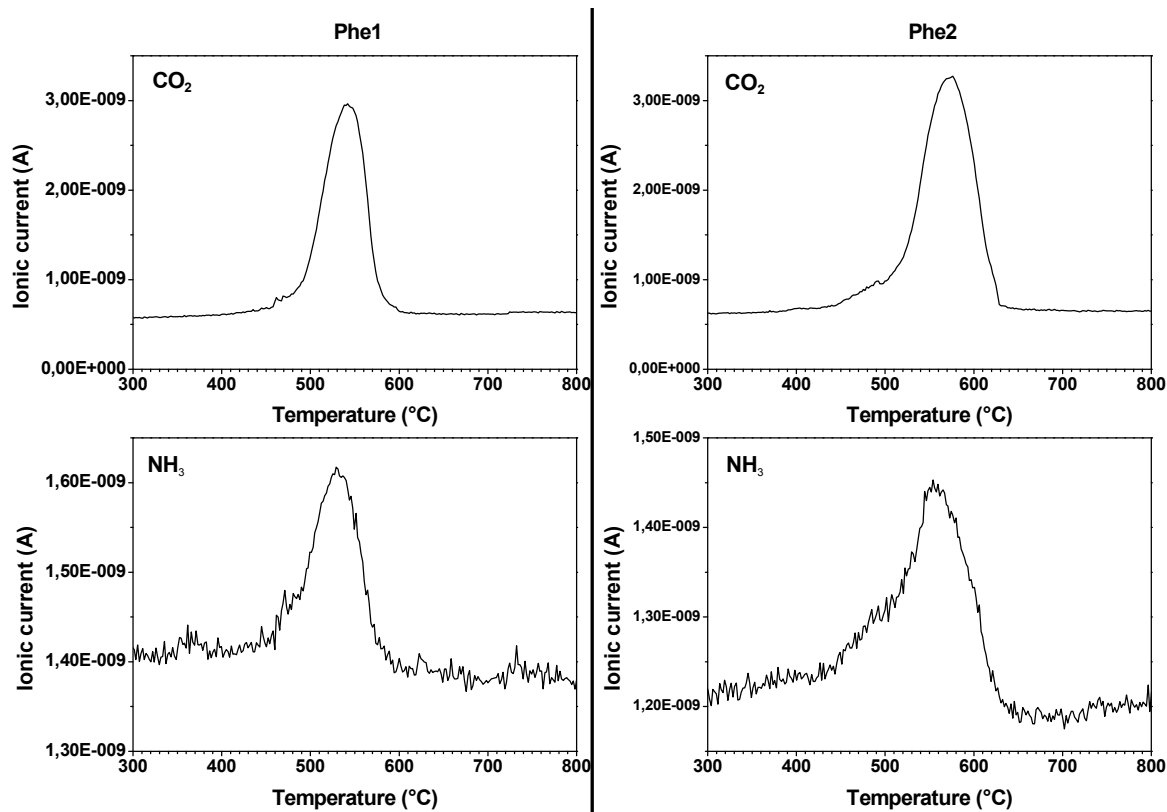


Figure 2: CO<sub>2</sub> and NH<sub>3</sub> MS signals for Phe1 and Phe2.

Figure 3 reports the signals related to organic molecules such as alcohols, phenols, toluene and benzene.

Decomposition of Phe 1 forms alcohols, whereas, besides alcohols, low molecular weight aromatics, i.e. benzene, phenols and toluene, are also observed in the case of the decomposition of Phe2.

The lack of aromatics with low molecular weight in the case of the decomposition of Phe1 is tentatively ascribed to the faster degradation observed by means of TGA analysis. It is proposed that for sample Phe1, besides alcohols that have been observed by MS, organics having higher molecular weight are produced, not detected by MS due to condensation in the capillary and/or in the furnace before reaching the MS detector.

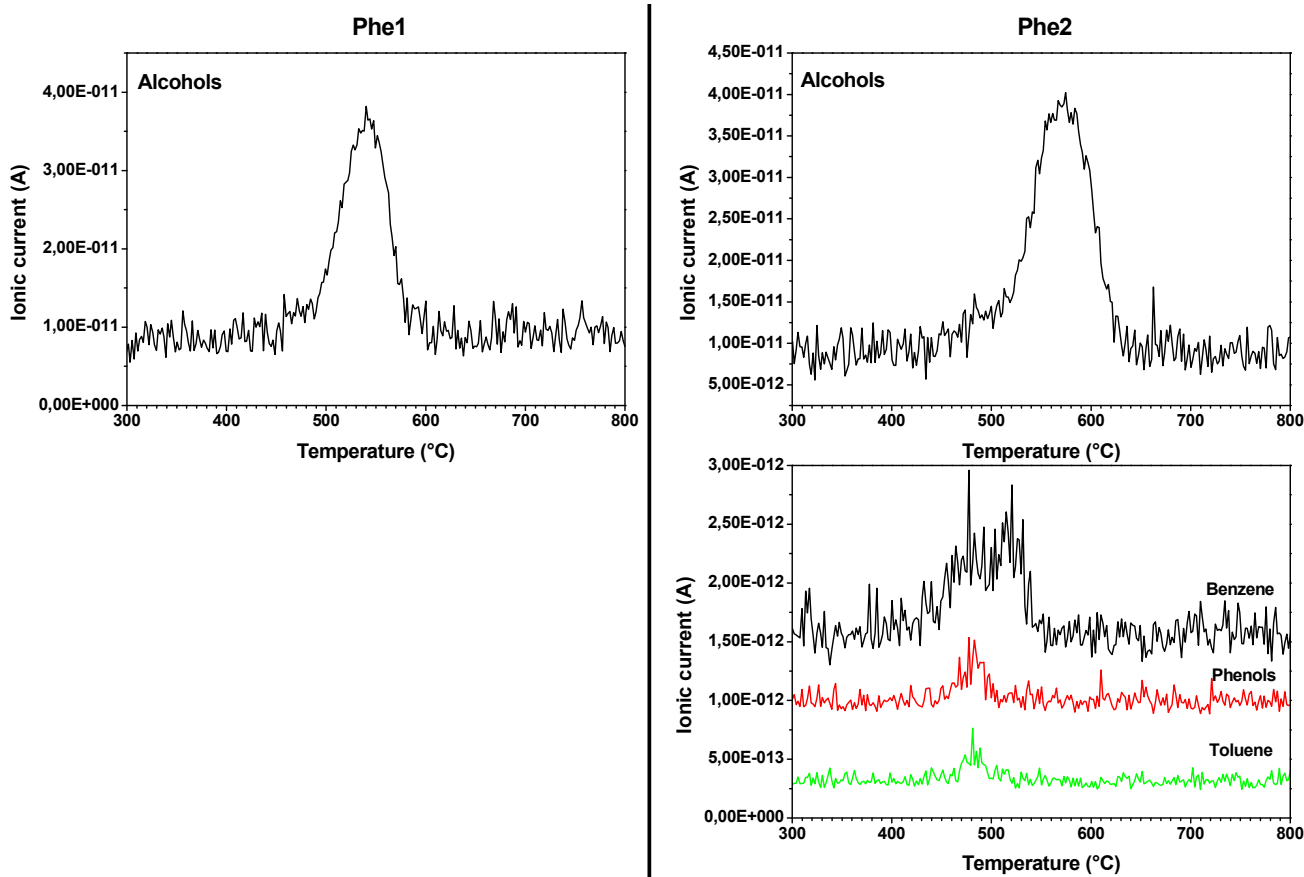


Figure 3: MS signals from the organic components for Phe1 and Phe2.

### TGA-MS in Argon

TGA-MS analysis were also carried out in inert atmosphere, i.e. Argon, in order to investigate the thermal degradation of the phenolic resins in absence of oxygen. The reason is due to the fact that, when a brake pad is in operating condition, it is in strict contact with another device, the braking disk, so that the working atmosphere may be poor in oxygen.

Figure 4 reports the TGA curves of Phe 1 and Phe 2 in Argon

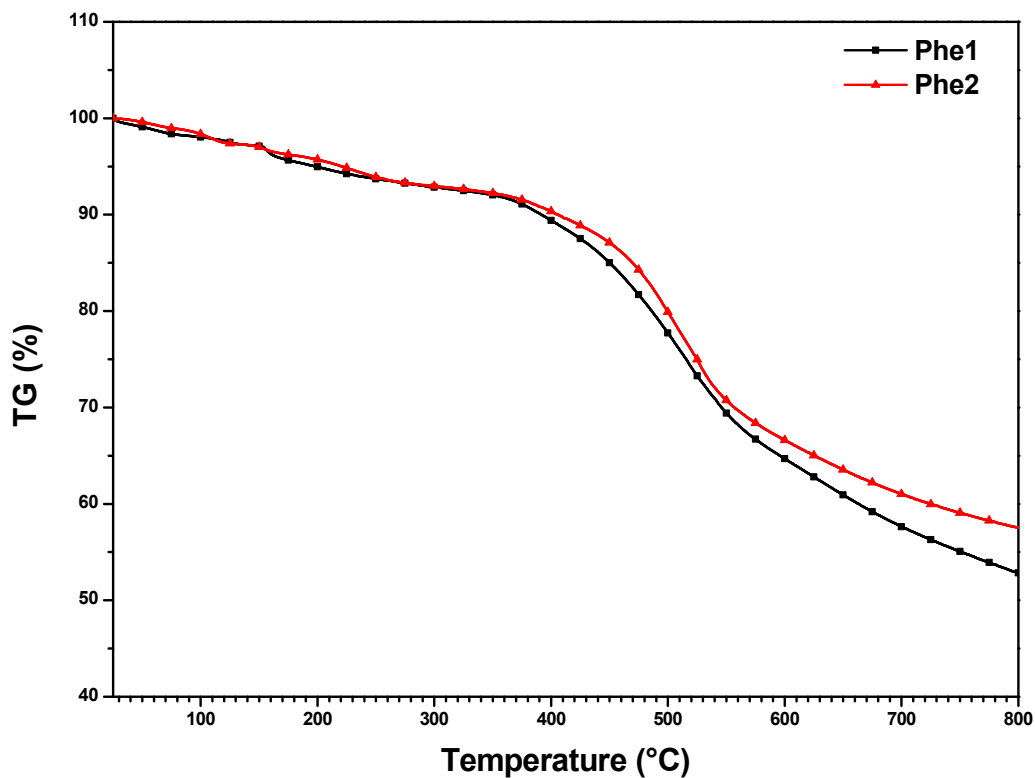


Figure 4: TGA curves of Phe1 and Phe2 in inert atmosphere

As observed for the degradation in air, the two resins show a similar behaviour. The main weight loss starts at the same temperature, that is close to 490°C. The total weight loss is slightly different, being that of Phe1 larger than that of Phe2 of about 5% of the total mass.

The residual chars of the two measurements were then analysed by FESEM (as discussed below).

A feature to be noticed is that Phe1 shows a small weight loss between 100°C and 200°C, which is not observed for Phe2. Corresponding MS data, reported in figure 5, reveal that the weight loss in this range of temperature is due to the release of  $\text{NH}_3$ .

Due to the toxicity of gaseous ammonia [5] and the low temperature of the release, this evidence is worth to be underlined.

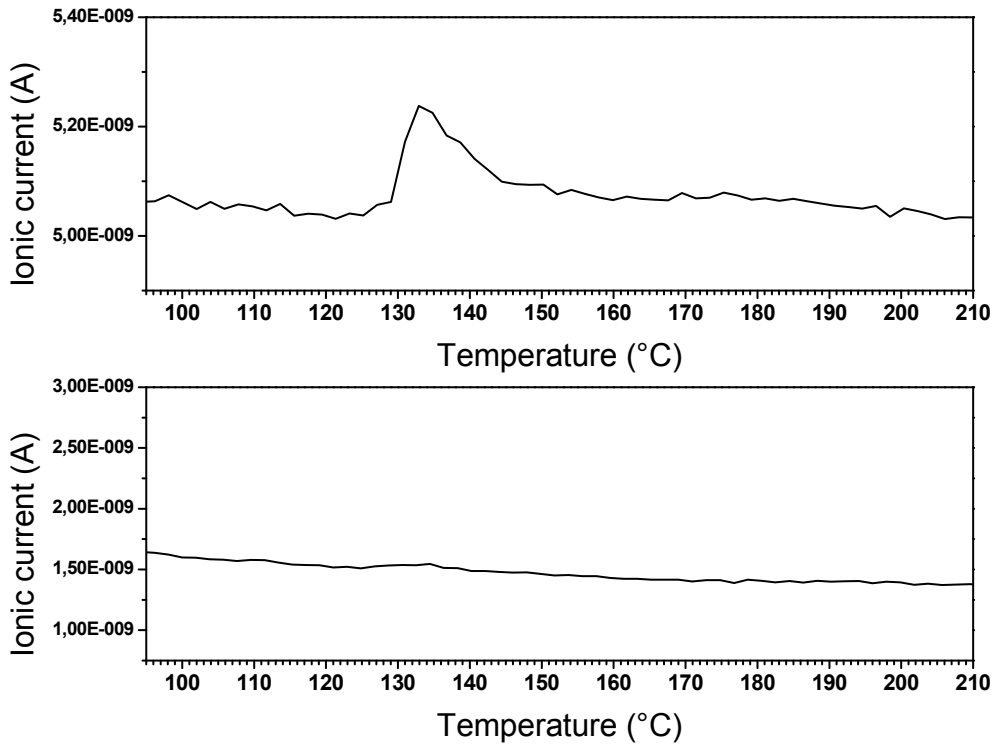


Figure 5: NH<sub>3</sub> MS peak for Phe1 (upper section) and Phe2 (lower section)

As expected, due to the absence of oxygen, no CO<sub>2</sub> release was observed for both samples.

At high temperature, at which the most significant weight loss occurred for both samples, MS revealed the release of organic species such as benzene and methane for Phe1, and methane and toluene for Phe2 (Figure 6).

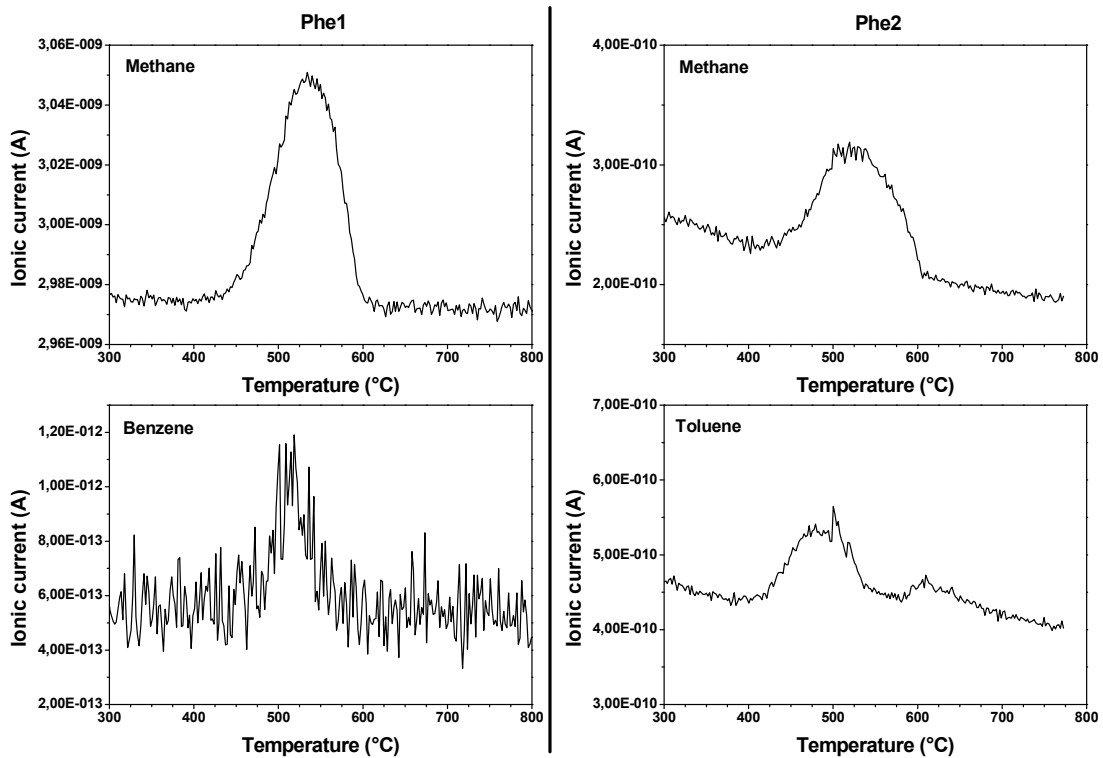


Figure 6: Organic compounds released from Phe1 and Phe2 in inert atmosphere



## FESEM on char from TGA in Argon.

The residual char obtained by the TGA measurement in Argon was analyzed by FESEM.

The pristine resins as such were also characterized, for comparison.

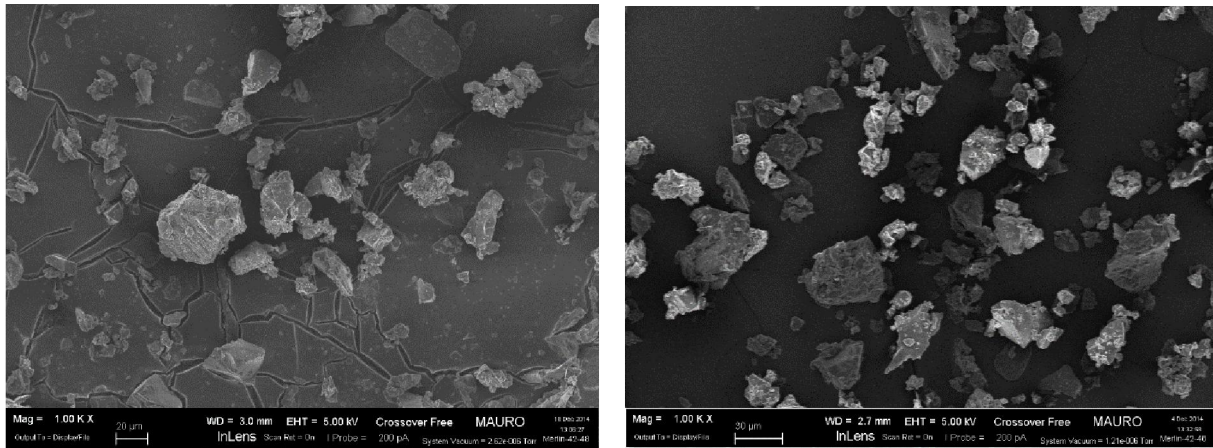


Figure 7: Resins (Phe1 on the left and Phe 2 on the right) morphology before TGA in Argon

Figure 7 shows FESEM micrographs of Phe1 (on the left) and Phe2 (on the right) as such. The two samples appear similar and in the form of heterogeneous particles having micrometer size.

The chars obtained from the two samples appear different and this is evident in particular at higher magnification (Figure 8).

The char from Phe2 appears compact, whereas the char from Phe1 is in the form of aggregates of nanoparticles having size of about 20 nm .

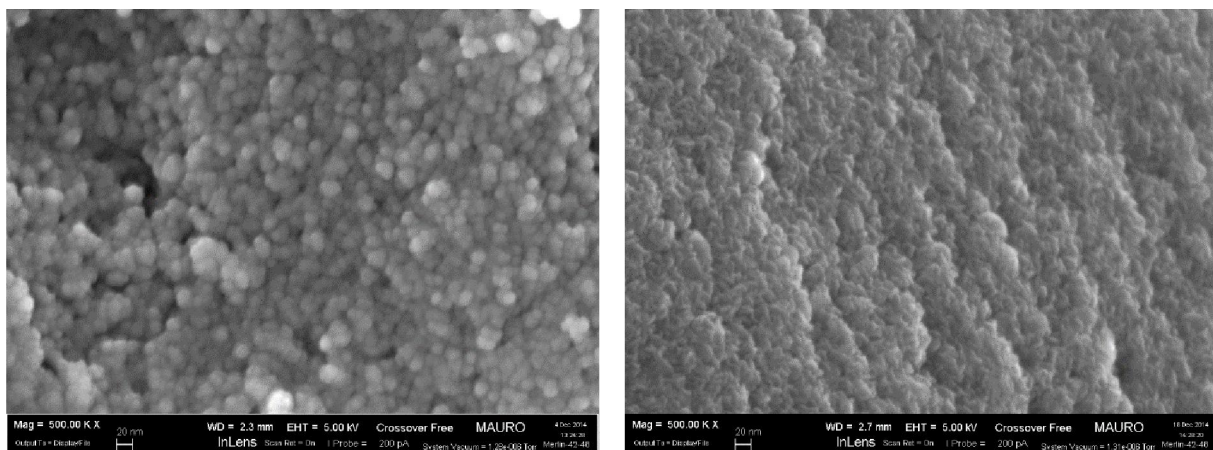


Figure 8: Resins (Phe1 on the left and Phe2 on the right) morphology after the heat treatment

## CONCLUSIONS

Qualitative tests on the degradation of two phenolic resins, commonly used in the brake pads industry, in the temperature range 25°C-800°C, were carried out by means of thermogravimetry coupled with mass spectrometry. Results show that, upon thermal degradation, phenolic resins release in the air gases such as CO<sub>2</sub>, NH<sub>3</sub> and organics aromatic pollutants (e. g. toluene and benzene), which can represent an environmental issue.

The degradation atmosphere strongly affects the released gases, as expected. CO<sub>2</sub> forms exclusively in presence of oxygen, whereas aromatics and ammonia have been released both in presence and in absence of oxygen (inert atmosphere, i. e. Argon).

Differences have been observed between the two phenolic resins, both in terms of amount and chemical composition of gases released, in particular under inert atmosphere.

The residual char after degradation in inert atmosphere has been also characterized by FESEM. The two resins formed chars with different morphology, being one more compact and the other made of aggregated nanoparticles with size of about 20 nm.

The whole set of data suggests that the gases formed by the thermal degradation of phenolic resins used in brake pads industry, as well as the char possibly produced by the degradation, can represent an environmental issue.

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