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Research onto use of New Textile Friction Composites in the Reduction of Non-exhaust Emissions

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Problems

Nowadays, one of the most important topics in context of environmental and health hazard research became airborne particles. Exposure to traffic-related PM plays an important role in the development of adverse health effects. Traffic-generated particles are associated with cardiovascular and pulmonary effects, as shown by both epidemiological and toxicological studies [1-8]. Some of these studies suggest that brake wear particles might contribute to these adverse effects [5,6]. Specific health concerns are related to the allergenity of tyre components such as Polycyclic Aromatic Hydrocarbons (PAH's) and latex, and the heavy metals used in brake linings. All of these compounds have toxic, mutagen attributes [9], but above all are respiratory sensitizers, inducing irreversible allergic reactions in the respiratory system.

Whilst exhaust gases in the road transport are already a concern for the European directives, there are currently no legal requirements for the control of non-exhaust particle emissions. Consequently, some of the approaches relating to non-exhaust particulate matter were highlighted [10]. Researches reveal that the traffic-related emissions are major sources of suspended PM in the urban areas [11-13]. Nevertheless, it can be claimed undoubtedly, that data relating to the physical and chemical properties, emission rates, and health consequences of non-exhaust particles derived from specific wear brake are uncertain/far from comprehensive.

Consequently a consistent knowledge concerning the effectiveness of the emission strategies is mandatory, in order to develop practical strategies for reducing the pollutant concentrations.

Three different technical approaches related both to vehicles and the infrastructure have been studied to reduce the emissions of PM:

- *Preventive controls* have been engineered to avoid material from being deposited onto the surface.
- *Mitigative* controls focused onto the removing any material that has been already deposited.
- "*Adaption*" to reduce exposure to the existing level of pollution.

Testing known amount of well-characterized brake wear particles, it was shown that:

- *Cleaning techniques* including high-pressure water washing in combination with vacuuming the road surface might be also efficient when it comes to collecting PM from the road surface [14-16].
- *Application of dust suppressants* can also be effective, but there are various disadvantages about the potential health and environmental impacts of the compounds used.

The abrasion elements, such as: brake wear, tyre wear and road surface wear have been evaluated as having dominancy, representing more than three quarters of the source strength of non-exhaust particles.

Starting from the idea the applicant has two major sustainable research expertise's, one being *knowledge of the cellulosic polymeric supports treatment against ageing process*, gained during the doctoral studies, and the other being a *higher comprehension of synthesis and characterization of nanoporous materials used in photo catalysis of organic pollutants* derived from textile industry wastewaters, during her post-doctoral activity, to reduce the emission of brake wear particles, the research proposes two novel directions tightly bound to her double expertise. These are (I) development of new ecological friction materials; (ii) collecting the brake particles as they are produced.

Characteristics of Coarse Fine and UFP Particles

According to their modes of aggregation, PM can be divided into:

- Aucleation mode generating *ultra-fine particles* (in the PM0.1 fraction), which can penetrate into the alveolar region.
- Accumulation mode giving "birth" to fine particles ranging between 0.05 μm and 2 μm in diameter).
- Coarse particle mode comprises particles with diameters in the size range between 2.5 μm and 10 μm contributing substantially to total aerosol mass [17,18].

The main constituents of these above *primary particles* are crustal elements (e.g. Si, Al, Ca, Fe), elemental carbon, and different organic compounds. *Secondary particles* are consisted of inorganic compounds (sulphates and nitrates) [19].

Physical and Chemical Phenomena Underlying the Brake Wear Process

Despite the fact that brake wear is recognized as a major source of traffic-related PM emissions, a deeper knowledge of the physical attributes and chemical composition of brake lining materials and particulate matter generated as a result of brake wear is uncertain [18].

Factors Affecting Brake Wear

A mechanically-induced wear meaning large frictional heat generation associated with wear is the results achieved when vehicle brake linings are subject to large friction during forced deceleration. Subsequently brake lining particles are released to the environment [20].

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A huge variety of brake pad compositions is available. For instance Filip P and his co-workers analysed the composition of 82 brake pads on the American market [21]. Also Garg found that at each stop the increasing of brake temperature induces a proportional increment of the mass of lost friction material: PM 10 and PM 2.5 emission [22,23].

Brake Composition

Generally speaking, the chemical composition of brake linings consists of four main components: *binders* (phenol-formaldehyde resins), *fibres* (metallic, mineral, ceramic, or aramide, including steel, copper, brass, potassium titanate, glass, asbestos, organic material, and Kevlar), *fillers* (barium and antimony sulphate, kaolinite clays, metal powders.) and *friction modifiers* with inorganic, organic, or metallic nature. Graphite is a major modifier used to influence friction, but other modifiers include cashew dust, ground rubber, and carbon black [24,25].

Brake Wear Particles

Physical properties

Particle size and number: From all of no exhaust emissions, TNO Institute of Environmental Sciences, Energy Research and Process Innovation, Apeldoorn, The Netherlands revealed a dominancy of around 90% (by mass) belonging to PM 10, whilst around 40-60% can be classified as PM 2.5, and up to 33% as PM 0.1. A significant fraction of airborne brake wear particles can be associated to PM 0.1 [26]. They also claimed that on average; around 35% of brake wear mass is released as airborne PM.

Particle composition: Investigating the chemical composition of both brake lining materials and emitted brake dusts from a range of commercial, heavy-goods vehicles, and trailers, using a combination of analytical techniques, such as: X-ray Fluorescence (XRF) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), a lot of reports have been emitted.

Thus, Kennedy and co-workers are discussing about concentrations of metals varying in terms of manufacturer and lining type, in some cases by several orders of magnitude [26]: iron (between 1% and 60%), copper (Cu 25% by mass) stressing the idea of the large variation in elemental composition of brake linings between manufacturers [27-30]. Dominant are also lead (Pb), cadmium (Cd), chromium (Cr), Cu, nickel (Ni), and zinc (Zn) being repeatedly reported to reveal their high concentrations in brake linings. Although a prohibitive fuel additive, Pb content of brake linings is high enough (12%), consequently brake wear emissions seem to picture a significant source of airborne Pb [30-32].

In Japan studies brought into attention levels of a few weight percent of: potassium (K), titanium (Ti), Cu, Sb, and barium (Ba). The occurrence of Sb in brake dust samples arises from the use of Sb as an alternative to asbestos in brake lining manufacture [31-34].

Using scanning electron microscopy and energy dispersive spectrometry to examine the morphological structure and elemental composition of brake lining material the studies revealed a noteworthy aspect: the brake wear process behaves only to reduce the size of the inorganic lining constituents relative to the original lining, whilst the chemical composition remains unchanged [35].

In terms of organic components, the identifiable portion of *the brake particle organics* consisted mainly of n-alkanoic acids (34.3%) and polyalkylene glycol ethers (56.9%), the findings suggest that only a small proportion of the organic content of brake linings and emitted as brake dust is extractable [36,37].

Sampling Methods

Laboratory-based brake system testing has the advantage that the collection efficiencies of wear debris tend to be high-90% or more, without significant particle losses to the surroundings, as opposed during on road operation.

Laser scattering method characterized brake wear particles concluding that wear debris tends to show a bimodal particle number size distribution.

Brushing brake dust samples from the inside of the rear drum brakes, consisting of suspension and filtration [38].

Brake dynamometer laboratory, in order to simulate "real-world" driving conditions [39,40].

Cascade impactor collected size-fractionated brake dust samples [32].

Subsequently the project proposes two main directions:

- development of new improved ecological friction materials;
- collecting/entrapping/destruction the brake wear particles as they are produced by photo catalytic methods (filters)

Rationale

Development of new friction materials as an alternative to asbestos fibres made brake pads arouse from the context of environmental and health hazard within global climate change. During braking asbestos could generate wear particles of different chemistries, released into the environment, with different potential of toxicity and mutagenity.

Moreover, there are various problems associated with asbestos due to its adverse effect on problem of life cycle assessment and waste management at the end of its service life. Since asbestos was banned, the number of its substitutes has been tested in formulations of the friction composites. The typical example is aramide fibers for the non-asbestos organic low-metallic (or nonmetallic) friction composites [41]. Nevertheless, aramide fibers are still of synthetic origin, being prepared by means of chemical synthesis [42], which could be hardly regarded as an environmentally friendly process.

At this juncture, the idea of asbestos replacement with friction materials having at least the same friction performance, given by its main attributes thermal, electrical, and sound insulation, inflammability has appeared. There have been trials to combine asbestos fibres with cement or woven into fabric or mats/ sheets [43,44].

Since worldwide, remarkable research is being done for the development of biodegradable polymers for various engineering applications [45,46], the research proposes plant fibres, such as sisal, jute, hemp, flax, to be used as reinforcement for different polymers in place of synthetic fibres (glass, Kevlar, carbon, etc.). Being renewable and biodegradable materials, cellulosic fibres are one of the highest valued alternative to be used as components in different kind of composites applications (e.g. kenaf fibers and betel nut fibers) [47-49]. Shalwan and Yousuf summarized the literature data and worked out a comprehensive review of the utilization of natural fibers as components in polymer matrix composites, also with a special focus on their tribological behavior [50].

The main demands these new friction composites for brake linings should fulfill are:

- Acceptable values of the friction coefficient.
- Stability at higher temperatures.

The most extremely serious aspect is the one regarding the thermal stability of the plant fibres. It is well known that hemicellulose decomposes from 220 to 315°C, and the most thermally stable is cellulose, which starts to decompose above 300°C and its decomposition terminates at 400°C [51]. In comparison with the most valued aramide fibers in terms of thermal stability, whose decomposition interval ranging from 400 to 450°C, these temperatures are lower [52].

Since, during intense braking, the temperature at the friction contact surface can locally exceed several hundred °C, the question is if the natural plant fibers can be used for application at such higher temperatures.

The proposal stresses the idea of increasing in the thermal stability of the plant fibres which will be used, by two main approaches:

- Increasing the content of cellulose, through removing the hemicellulose and lignin content by an alkaline procedure.
- The improvement of thermal stability of the new obtained friction polymeric composites using Montmorillonite (MMT) emulsion, which is a type of inorganic natural clay containing SiO4 tetrahedral sheets arranged into a two-dimensional network structure, and might provide thermal resistance [53].
- The other research approach is the direct growth of pure and doped nanostructured ZnO coating onto the above mentioned fibrous polymeric support as active photo catalyst material in air purification reactors.

Impact

The expected results will be a valuable addition to the knowledge in the field of novel materials with friction performance, because ecological friction materials are in its infancy. This research might open a broad field of technological applications, due to their cost and low environmental impact of the eco-pad, with potential commercialization in future.

The newly developed eco-pad will be non-asbestos, non-metal, and non-aramid friction materials, which meets all the developing trends of the modern friction industry.

In terms of *the second research direction*, the expected impact is to make accessible new scientific information regarding photo catalytic materials on polymeric support, in order to capture/block/entrap the emissions of brake wear particulate matter, where this kind of knowledge is uncertain.

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