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Investigation on the recyclability potential of vehicular brake pads

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ABSTRACT

In this work, different fractions of material recovered from exhaust brake pads were mixed with a masterbatch used to produce low-metallic brake pads. The materials to be recycled came both from the friction material and the underlayer of the brake pad to assess the recycling of all the composite part of the exhaust brake pads through an end milling process. The tribological tests implemented on the pins demonstrated the technical feasibility of this recycling approach in a cradle-to-cradle perspective. A full mechanical characterization provided important indications for selecting the more promising compositions. Compression strength of the reference pins was retained up to a 30 wt% concentration of the recycled material; while above this value, a decrease in both the stiffness and the failure resistance was observed. Pin-on-Disc tribological tests on recycled pins containing powder recovered from the pad *underlayer* only highlighted an unstable and higher friction coefficient and specific wear coefficient with respect to the reference friction material. On the contrary, the wear behavior of the pins prepared using just recycled *friction material* was very close to that of the reference sample, as concerns the emission behavior of the particulate matter produced by the wearing out of the tribological samples.

1. Introduction

The main concerns on vehicular traffic pollution are mainly associated with exhaust emissions from internal combustion engines. Over that latest decades, car manufacturers have developed several strategies for the improvement of engine efficiency and better emission control systems, as well as the introduction of hybrid or electric mobility, in order to reduce, or fully eliminate, this kind of emissions. On the other hand, there are other vehicular emissions produced by non-exhaust sources, which are not affected by this ongoing drive substitution. This is the case of brake systems, tires and related road asphalt. Non-exhaust emissions are becoming relatively more important, both for the mentioned exhaust reduction, both their pervasive character and significant impact on the environment and human health. Of course the progressive widespread diffusion of hybrid and fully electrical engine vehicles will render non-exhaust emissions predominant, reinforcing the interest for an adequate management of this issue [1].

Among non-exhaust sources, the wearing out of the brake parts, i.e., discs and pads, represents a significant contributor to airborne particulate matter (PM), notably in urban areas featuring high traffic density and, thereby, braking frequency. Several studies have demonstrated that the contribution to non-exhaust traffic related PM_{10} emissions by the brake wear derived particles is ranging between 16 and 55 wt%. These emissions sum up to 11–21 wt% of the total (engine exhaust included) traffic related PM_{10} emissions and, most importantly, contribute particular pollutants, requiring specific safety regulations, like heavy metallic elements [2]. According to the United Nations Economic Commission for Europe (UNECE), over the last decade the total amount of copper emissions from all sources (road transportation, industrial processes, etc.) have been estimated in 4.0–5.5 ktonnes/year on the European continent only, with a contribution from brake wear of 40–60 wt% in the urban areas [3]. These percentages are to be regarded as rather critical, considering that the World Health Organization (WHO) has launched warnings on the specific role of metallic components, like copper, zinc and manganese, as concerns several adverse health effects of PM from vehicular traffic [4]. A close relationship between the concentrations of such elements and mortality from cardiovascular and respiratory diseases and from lung cancer has been envisaged and statistically validated. In view of this threat, on January 21st, 2015 the US Environmental Protection Agency (EPA), the United States of America Government, and the

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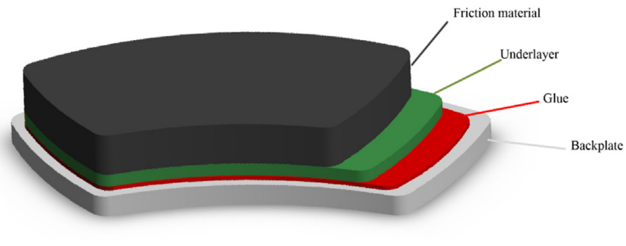


Fig. 1. Schematic of the different layers in a brake pad.

automotive industry signed an agreement aiming at reducing precisely the use of copper in vehicle brake pads: the so-called “copper-free brake initiative”, calls for reducing copper in brake pad friction materials to less than 5 wt% by 2021, and less than 0.5 wt% by 2025 [5].

Improving the quality of brake PM emission, within the more general task of reducing this contribution to airborne PM, is strictly related to establishing a virtuous life cycle for this mass product. This is precisely the focus of the present study, which presents a recycling strategy for the material obtained from worn out brake pads, to be used to produce friction material still interesting for the manufacturing of brake pads, in a cradle-to-cradle perspective.

The friction material, of which the top layer of a brake pad is made, must comply with some essential requirements: a stable friction coefficient in combination with a sufficiently high mechanical strength and temperature resistance, to cope with typical operational conditions. In addition to these materials properties, comfort during braking and reduced noise emission should be considered, as important target features of the component [6].

At the present time, recycling procedures are largely adopted for other parts of a brake system, like brake-calipers and discs, typically made of aluminum alloys and cast iron, respectively, so that traditional metal casting technologies can be adopted straightforwardly. As concerns brake pads, the current approach is to replace them at the end of their useful lifetime and to send them to metallurgical plants, as scraps for electric arc furnace (EAF). For the sake of completeness, it must be said that landfill disposal is another, although on smaller bases, destination for used brake pads. The drawback of the EAF based approach is that residual friction material together with underlayer components, still present on pad substitution, are source of substances released as gaseous polluting agents in the atmosphere [7]. Since, an estimated one third of the original pad material is on average still there in worn out pads, the relevant emission may be significant, even because usually not appropriately abated by the plant filters, since not specifically designed for this kind of emissions. The possibility of removing the residual friction material becomes therefore an interesting option, also as a first step for the smart management of the residual brake linings, which may provide a large amount of raw materials (RMs), considering that each year about 75,000 tons of used friction material from the worn brake pads are accumulated and disposed in landfills or alternatively partially smelted to low quality steel [8]. The selective separation of the friction material residues from the metallic backplate can be achieved by high temperature thermal decomposition of the adhesive layer between the pad top layer and the backplate itself. Alternatively, the embrittlement of the brake lining can be induced by immersion of the used pad into a liquid nitrogen bath, helping the subsequent detachment by applying mechanical stresses [9].

In a similar work, Yezhe at al [10]. Investigated the recycling of worn out brake pads through crushing and ball milling of worn friction material and adding 8% of phenolic resin to the resulting batch. The results of the wear tests indicated comparable performances as those of the virgin material. However, in this study, the management of the pad underlayer was not considered since the friction material only was considered in the production of the recycled material.

For designing an effective recycling method of worn out brake pads owing to their multilayered composite structure, it is important to address a way to detach the friction material from the underlayer. The underlayer is placed in between the friction material and the backplate with the main purpose to damp vibrations originating at the disc-pad interface [11]. It is typically made of a rubbery material with properties rather different from those of the friction material, playing a key role in the braking performances of the whole pad (Fig. 1).

Table 1
EDXS analyses of the “reference” masterbatch and of the recovered, from worn pads, friction materials.

Element	Reference	Worn Pads
Oxygen [O]	12.9	14.9
Sodium [Na]	0.7	–
Magnesium [Mg]	2.1	10.6
Aluminium [Al]	2.2	5.5
Silicon [Si]	1.3	2.0
Sulfur [S]	1.0	4.7
Phosphorus [P]	–	0.5
Calcium [Ca]	0.6	1.8
Chromium [Cr]	1.2	1.4
Iron [Fe]	48.9	20.3
Zinc [Zn]	2.9	1.8
Tin [Sn]	1.3	6.2
Carbon [C]	24.9	30.2

A sustainable recycling route should consist of a low-cost process for the production of new components. The present work will explore the feasibility of recovering of the brake linings by means of a relatively quick and cheap mechanical removal of the friction material at room temperature.

The materials obtained from used brake pads will be employed as fillers in the production of new friction materials, starting from a virgin powdered masterbatch with composition corresponding to a low metallic copper-free friction material. The RMs recovered from the used brake pads comprise both the friction layer and the underlayer. To assess the actual potential of the resulting mixtures as brake friction material, tribological pin-on-disc (PoD) tests were conducted. The new pins and the products of the wear tests have been analyzed, as concerns their microstructural, mechanical and tribological features.

This work is part of a research activity carried out in the framework of the ECOPADS (Eliminating COpper from brake PADS and recycling) EU project, which intends to provide the design of a complete recycling procedure for brake pads linings. Another main task of the Project is to anticipate the forthcoming standards and regulations concerning brake emissions and limitations to the usage of toxic and environmentally detrimental components, e.g., copper.

2. Experimental procedure

2.1. Materials

2.1.1. Reference material

The reference friction material for this work was of a commercial low metallic copper-free type, for brake pad manufacturing, provided by Brembo S.p.A (Bergamo, Italy). This material has been supplied as a masterbatch with all the ingredients of the brake linings, homogeneously dispersed: the reinforcement fibers, the friction modifiers, the various fillers and the phenolic resin, this latter to be cured during the sample production. Worn pads were also provided by Brembo S.p.A for the extraction of the recycled friction and underlayer material. These pads belong to three different commercial copper-free compositions. Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDXS) analyses of the masterbatch and worn pads recovered friction materials are presented in Table 1 and Fig. 2.

2.1.2. Recovery routes

The mechanical removal of the residual material from the worn out

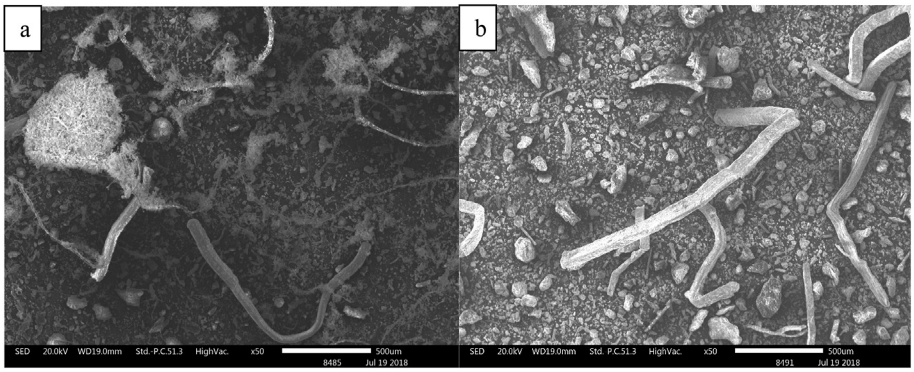
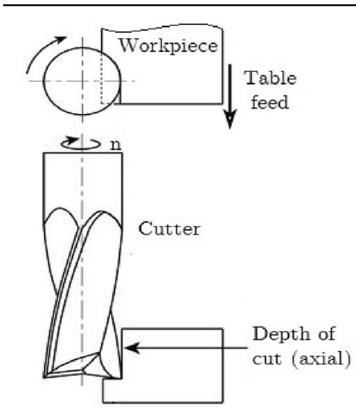


Fig. 2. SEM images of (a) reference masterbatch powder and (b) powder mix obtained from the worn pads after grinding.

Fig. 3. End-milling used for the selective recovery of the friction material and underlayer from the worn pads.

Table 2
Details of the end-milling process used to remove selectively the brake lining from backplate.



End-Milling Parameters	
Table feed	115 mm/min
Spindle speed	160 rpm
Axial depth of cut	1.5 mm
Cutter Characteristics	
Diameter	20 mm
Number of flutes	3
Angle of twist	30°

brake pads was pursued via end-milling, which is regarded as a route, which can be scaled up to industrial level, considering its rapidity and relatively low cost, even in view of an automatic management of this material removal operation (Fig. 3). The approach has been adopted both for the selective removal of the outermost region of the brake lining, i.e., the friction material, and of the rubber-rich underlayer adherent to the backplate, which is actually tougher and thereby more difficult to remove. The machine parameters used during the selective separation via end-milling are given in Table 2. During this first recovery step, particular care was devoted to removing the friction layer only. This was made not to pick up the 2–3 mm thick underlayer, which was indeed separately removed from the backplate, using the same end-milling procedure.

2.1.3. Selection of the compositions

A *friction material*, the top layer of an automotive brake pad, is normally produced by hot compaction of a powder mix, with thickness ranging from 10 to 13 mm. The components of such mixture are generally classified in five main groups: binder (generally a thermosetting phenolic resin that holds together the different components), reinforcing fibers (in order to provide mechanical strength), abrasives (like alumina, zirconium oxide, silicon carbide, zircon), lubricants (like graphite and metal sulfides), able to stabilize the friction coefficient, and mineral fillers (i.e., vermiculite, mica, barite, calcite and fluorite), mainly added to improve the manufacturability and reduce costs. Another layer of the brake pad stack is the so-called *underlayer*. It is the pad section below the outermost friction material, with a thickness of 2–3 mm approx. The chemical composition of the underlayer material is rubber based, since its primary role is to reduce the transfer of squeal noise, i.e., the unwanted high frequency vibrations generated during braking. The underlayer also acts as a thermal barrier against the heat generated during the dissipation of the kinetic energy at braking, flowing through the friction material toward the metallic backplate. Eventually, a larger rubber and resin content is meant to ensure adequate shear strength and cutting resistance of the brake pads.

Friction materials obtained from three different brake linings ("recycled material" in the following), having different compositions,

Table 3
Composition of the developed formulations.

	Weight Fraction [wt.%]							
	Reference	F-formulations				U-formulations		
	REF	F25	F50	F75	F92P8	U10	U20	U30
Masterbatch	100	75	50	25	–	90	80	70
Friction Material (F)[a]	–	25	50	75	92	–	–	–
Phenolic Resin (P)[b]	–	–	–	–	8	–	–	–
Underlayer (U)[c]	–	–	–	–	–	10	20	30

[a] (F): mix of the recycled friction materials.
[b] (P): virgin phenolic resin.
[c] (U): mix of the recycled underlayer materials.

were mixed together, to reproduce a situation faced in a real industrial process, where brake pads from different Producers have to be managed. In order to investigate the effect of different percentages of recycled material powder on the mechanical and tribological performances of the resulting friction materials, also in comparison with the reference lining, different formulations were prepared. F-formulations are composed of 25, 50 and 75 wt% of recycled material mixed with a masterbatch dose necessary to reach 100%. An additional sample codenamed F92P8 was prepared. It is made of 8% virgin phenolic resin (P) mixed with 92 wt% of recycled friction material. This composition was prepared to evaluate the possibility of using recycled friction material only. U-formulations were made of 10, 20, 30 wt% of recycled material obtained from the underlayer only, added to relevant parts of masterbatch powder. The composition of all the formulations developed and analyzed in this work are given in Table 3 s.

2.2. Pin preparation

Each powder mix in Table 3 was mixed up with a WAB Turbula® T2F shaker-mixer for 10 min to ensure a complete homogenization. For the preparation of each single pin, about 2 g of powder mixture were tap-pressed into a cylindrical mold of a hot-pressing apparatus. After a sequence of four pressure ramps up to 7 MPa, needed for a complete degassing of the powder, each specimen was kept for 7 min inside a hot mold under a pressure of 5 MPa and a temperature of 150 °C. The pins were subsequently post-cured in an industrial oven for 7 h at 200 °C. In this way, nine cylindrical pins of 10 mm in height and 10 mm in diameter were obtained for each powder mix composition (see Table 3).

2.3. Characterization

2.3.1. Density of the pins

The bulk density of each pin was evaluated as the ratio of its mass to its volume. Three measures of the diameter and three measures of the height were performed on each pin using a digital Vernier caliper with a sensitivity of 0.01 mm, to obtain average values used for the calculation of the pin volume, assuming the specimens as perfect cylinders. The mass was measured with a precision scale having a 0.1 mg sensitivity.

2.3.2. Shore D hardness

According to the ASTM D2240 standard, the Shore D scale was used for the measurement of the hardness of the samples with the application of a vertical force of 44.64 N. Before each measure, the pins were grinded with a SiC 500 grit abrasive paper in order to ensure a flat and parallel surface of the base planes, as required by the standard. Three cylindrical pins for each formulation were tested, measuring five values of the hardness in different positions on each specimen's surface.

2.3.3. Compression test

The compressive strength of the samples was evaluated through uniaxial tests carried out on the pin samples, using a universal testing machine, Instron 5969, equipped with a load cell of 50 kN. For each formulation, three pins were tested at constant compressive-strain-rate, by imposing a cross-head speed of 1 mm/min. Prior to testing, as for the hardness tests, the pin base planes were grinded with a SiC 500 grit abrasive paper for a better contact. The compressive strength was recorded as the maximum stress sustained by the samples, determined by dividing the maximum load by the cross-sectional area in unloaded conditions, as indicated in ASTM E9-09. The compressive elastic modulus was evaluated following the ASTM E111-17 standard, from the stress and, corresponding, strain increment in the elastic regime of the stress-strain curve.

2.3.4. Pin-on-disc tests

A Biceri wear rig pin-on-disc (PoD) tribometer was used at room temperature to perform the tests based on ASTM G99 standard. A pearlitic grey cast iron (codename: GLH31) disc was used as counterface. The testing parameters (sliding velocity of 1.57 m/s and a nominal contact pressure of 1 MPa) were selected based on previous investigations [12,13]. The duration of each test was 90 min, after an initial running-in period of 30 min, needed to reach a steady state tribological regime. The friction coefficient (μ) was constantly recorded during the tests, as the ratio between the tangential force required to restrain the pin and the normal force pressing the pin against the rotating disc [14]. The specific wear coefficient (K_a) was calculated using Eq. (1):

$$K_a = \Delta V / F_n S \quad (1)$$

where ΔV [m^3] is the wear volume, during the PoD test, F_n [N] is the normal applied force and S [m] is the sliding distance.

2.3.4. Evaluation of emissions

The study of the emissions was performed following the test method developed by Olofsson et al. [15], using the PoD tribometer equipped with an Optical Particle Sizer (OPS). The OPS (TSI OPS 3330 instrument) is a portable equipment that provides an accurate measurement of the particle concentration using a single particle counting technology based on light scattering. This instrument is sensitive to particles with a size larger than the wavelength of light, i.e., from 0.3 to 10 μm. In order to control the airborne particle matter (PM) contribution from the surrounding environment, a closed chamber has been installed over the tribometer, with a clean air supply to ensure the measure of the wear particle generated by the pin/disc sliding only, as illustrated in Fig. 4.

2.3.6. SEM observations

Scanning Electron Microscope (SEM), model JSM-IT300, equipped with an energy dispersive X-ray spectroscopy (EDXS) system and operating at 20 keV accelerating voltage was used to analyze the surface morphology of the worn pins and to evaluate the composition of the investigated regions.

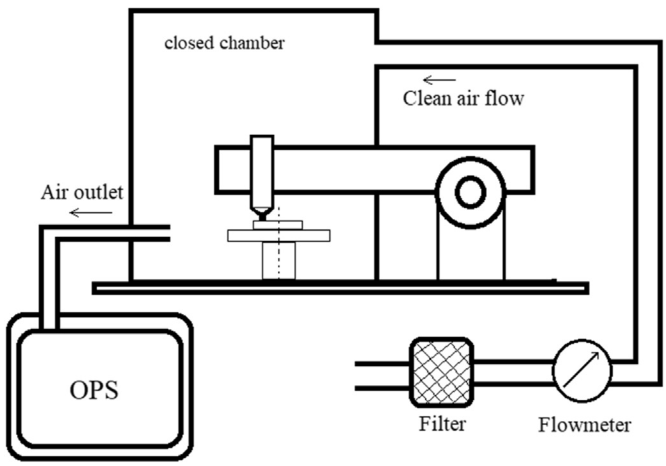


Fig. 4. Scheme of the test equipment for the analysis of the emissions.

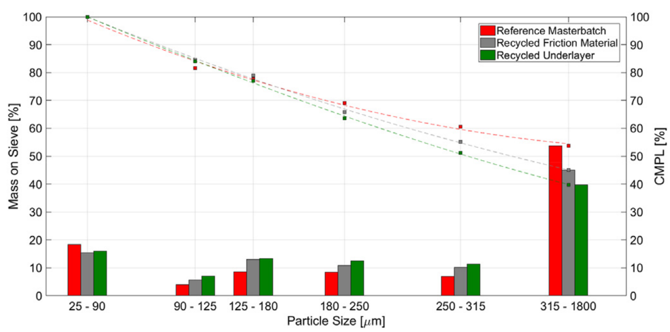


Fig. 5. Particle size distribution after sieving: the reference masterbatch, the recycled friction materials and the underlayer, as extracted from the used brake pads. Bars: percentage of the mass fraction; dots: cumulative mass percentage larger (CMPL) than the relevant sieve size.

3. Results and discussion

3.1. Particle size distribution

Fig. 5 shows the analysis of the particle size distribution, as obtained upon sieving the end-milling removed products, i.e., friction material and underlayer from the brake pads, according to the ASTM D4513-11 standard. All values are normalized by the total weight of the mass for each sieving stage. The bar plot gives the mass percentage values of particles with size in the specified ranges. Data points refer to the cumulative mass percentage of powder larger (CMPL) than the relevant sieve size. From Fig. 5, it turns out that particle size distribution of the reference masterbatch is substantially similar to that of the recycled friction material and of the underlayer end milling machined on removing them from the backplate. Therefore, owing to the comparable particle size distribution as that of the reference masterbatch, it was decided to proceed directly with the preparation of the powder mixes, containing different percentages of the recycled and reference masterbatch (see next section).

3.2. Density

The density values of the recycled pin materials, compared to the reference's, are shown by Fig. 6. It can be observed that the addition of the recycled powder, either friction material or underlayer, does not reduce the density of the relevant samples. Both U- and F-formulations show slightly higher density with respect to the reference sample. Only the F92P8 material has a lower density, a result which is in agreement

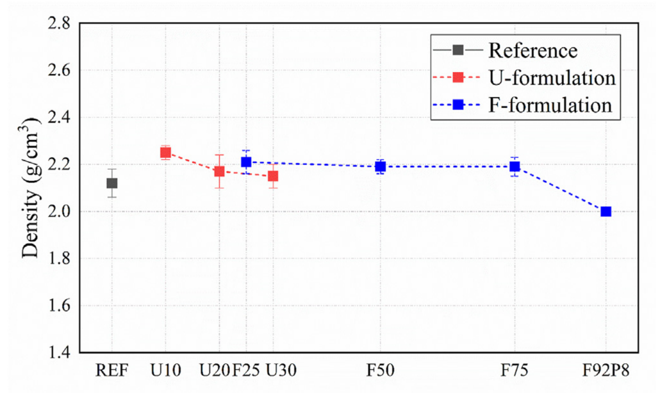


Fig. 6. Trend of the density of pins containing different amounts of recycled brake pad material.

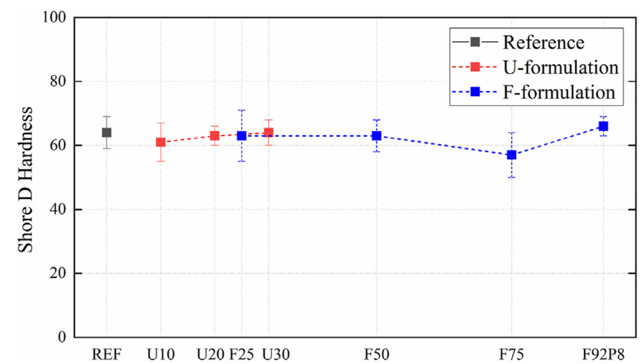


Fig. 7. Shore D hardness of pins with different amounts of recycled brake pad materials.

with the addition to this particular mix of 8 wt% of phenolic resin. Density values are compatible with those obtained with similar compositions considered in previous investigations [12,13,16], being the minor differences to be ascribed to the pin preparation procedure, with particular regard to the powder degassing treatments.

3.3. Hardness

Fig. 7 shows the mean values of the Shore D hardness of the different friction materials. It can be seen that the mean values of hardness are nearly constant in all samples. This result can be taken as an interesting result, considering that one of the scopes of this study is to compare properties of friction materials featuring different composition, particularly as concerns the content of recycled brake pad material.

3.4. Compressive strength

The compressive stress-strain curves for the F- and U-formulations are shown together with the reference (REF) material curve in Fig. 8a) and b) respectively. Below a recycled fraction of 25 wt%, the material strength does not significantly vary with respect to the reference material. As concerns the addition of recycled underlayer material, it does not affect the compressive strength of the REF sample (Fig. 8b). Most likely, the higher amount of the polymeric compounds are able to counterbalance the brittleness related to some components of the recycled materials, e.g., cured resin fragments, possibly embedding different constituents.

Fig. 9a shows the compressive elastic modulus of the different samples, measured from the relevant compression curves. A reduction in elastic modulus takes place when the recycled powder is added to the original masterbatch, particularly at elevated concentrations (i.e., F50,

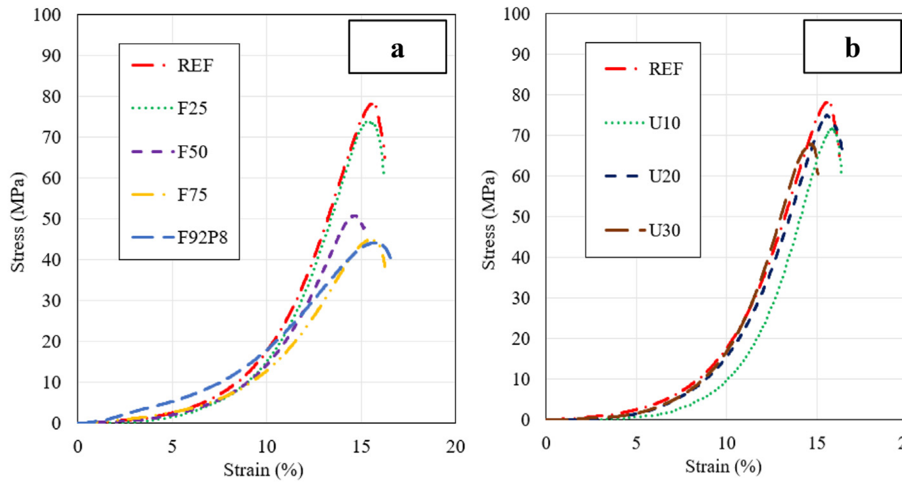
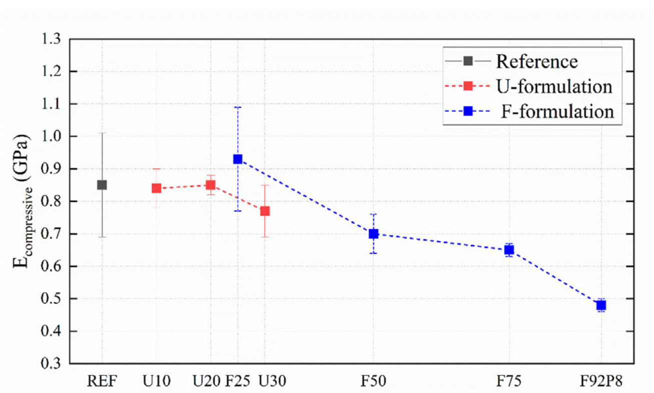
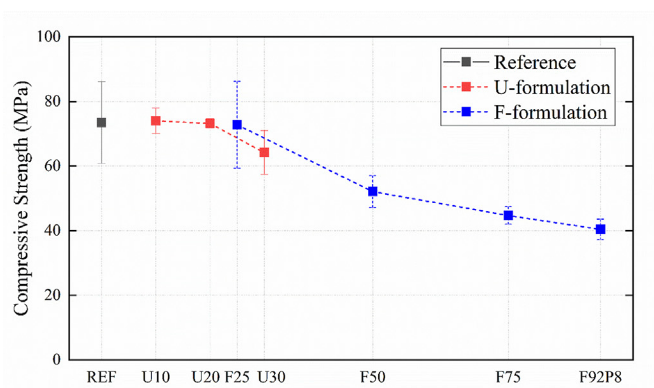


Fig. 8. Compressive stress-strain curves of pins containing different amounts of (a) recycled friction materials and (b) recycled underlayer powder.



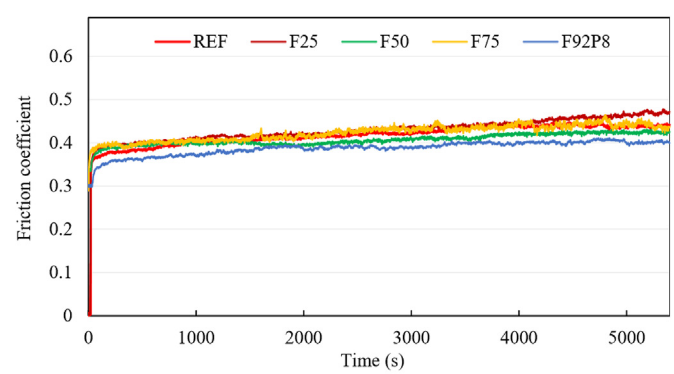
(a)



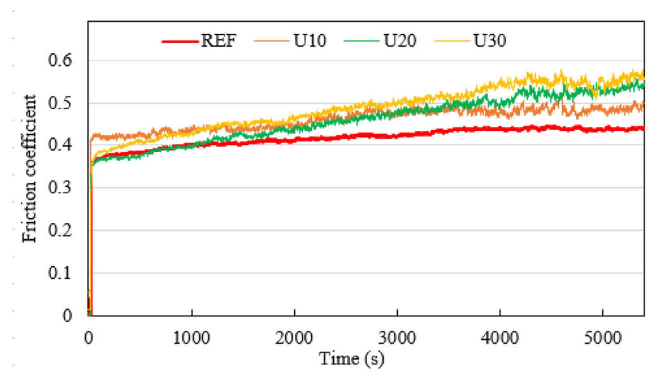
(b)

Fig. 9. Trends of (a) compressive elastic modulus and (b) compressive strength from compressive tests on pins with different concentrations of recycled, both friction (F) and underlayer (U), materials. The values for the reference material are also shown.

F75 and F92P8 samples). When the recycled material fraction in the original mixture overcomes 25–30 wt%, the progressive reduction in compressive elastic modulus may be a critical issue regarding the noise, vibration, and harshness (NVH) properties of the brake system. Indeed, this result does not meet the need to keep a high compressibility in brake lining in order to reduce the squeal noise generation [17,18]. Thus, it is to be expected that in case a friction material with a recycled fraction higher than the limit of 25–30 wt% is used, the other components of the brake system, e.g., backplate, caliper, etc., should provide an adequate dissipation of the squeal noise and damping of the mechanical vibrations during braking. Fig. 9b shows the compressive strength of pins with different percentage of recycled materials. The compressive strength of the samples decreases with the increase of the recycled fraction. The values of the compressive strength of samples containing up to 25 wt% of recycled materials are compliant with the values reported in the works on brake pads containing $CaCO_3$ and palm slag as filler materials in their composition [19,20]. It must be highlighted that all the developed



(a)



(b)

Fig. 10. Friction coefficient versus time curves from PoD tests on (a) F-formulation and (b) U-formulation samples, compared to the reference (REF) material.

Table 4
Specific wear coefficient of the prepared samples after 90 min of PoD test.

Sample	K_a [10^{-14} m^2/N]
REF	2.70 ± 0.88
F-formulations	
F25	2.89 ± 0.79
F50	2.83 ± 1.29
F75	2.96 ± 0.66
F92P8	3.33 ± 1.13
U-formulation	
U10	3.71 ± 0.45
U20	4.26 ± 0.82
U30	4.93 ± 1.37

formulations are characterized by a strength four times higher than 10 MPa, which is the pressure developed during a hard braking in standard, no heavy duty, road vehicles [21].

3.5. Wear

Fig. 10 a) and 10 b) show the evolution of the friction coefficient during PoD tests during 90 min for all samples sliding against a grey cast iron disc. There is a similarity among the friction coefficient of the reference sample and those of the recycled materials. Comparing Fig. 10a), referring to the F-formulations with Fig. 10b), the friction coefficient of the U-formulations, it can be observed that both the trend and the level of friction coefficient are affected by the type of recycled powder: either underlayer or friction material. According to Fig. 10a), the values of friction coefficient for the REF sample and F-formulations are all compliant with those obtained in companion studies involving commercial brake friction materials [12,22,23]. On the contrary, the behavior of the U-formulations (Fig. 10b) is quite different. Considering the larger rubber content in the recovered underlayer material added to the masterbatch powder, the friction coefficient stabilizes after a longer testing time reaching a higher value (mean value 0.52, to be compared with 0.43 of the REF material). Moreover, the addition of underlayer material causes a larger scatter of the friction coefficient during the PoD test, most likely due to a heterogeneous material microstructure. In the quoted study on recycling of worn out brake pads [10], a higher friction coefficient (average of 0.55) was reported for recycled brake pads with compositions similar to F92P8 sample.

The specific wear coefficient (K_a) can be taken as an indicator of the severity of wearing out during the sliding contact between the pin and the rotating disc. The mean values and the relative standard deviations of K_a are listed in Table 4. By far, the most important consideration is related to the attainment of mild sliding wear conditions [24]. As emerges from the data in Table 4, samples with F-formulations are all characterized by specific wear coefficients close to that of the REF material, and therefore relatively promising in view of real applications. On the other hand, the U-formulations have quite larger K_a values, a result that would confirm the poorer quality of these materials, as inferred already by the evolution of the friction coefficient (Fig. 10b)).

3.6. Emissions

Fig. 11 shows the results of the particle emission for samples F25, F75, F92P8, U30 compared to that for the REF sample. It turns out that on replacing 25 wt% of masterbatch with recycled friction materials (F25) the level of emissions raises from 208 particles/cm^3 of the REF to 311 particles/cm^3 of the F25 material. A higher fraction of recycled material, i.e., 75 wt%, results in an even higher emission rate. These results are coherent with the relevant trend of the wear rate coefficient, as evaluated from the Archard's law (Eq. (1)): the larger the wear rate the higher is the emission (see Table 5). Just one data point has been acquired for the U-formulations, considering the relatively poorer quality of this material, as

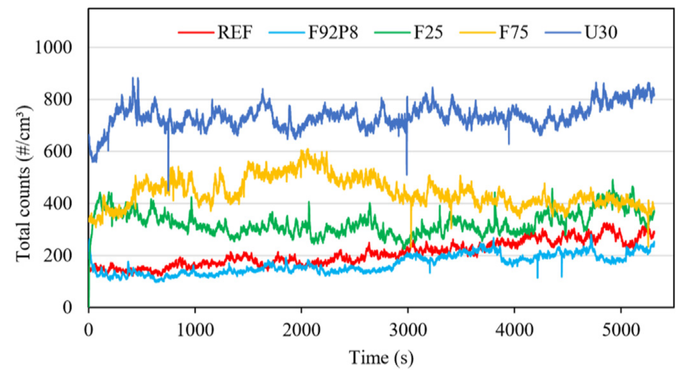


Fig. 11. Mean values of particles emitted during PoD tests on REF, F92P8, F75 and U30 samples.

Table 5
Emissions measured during the PoD tests on REF, F92P8, F75 and U30 samples.

Sample	Total counts (#/cm^3)
REF	208 ± 52
F92P8	189 ± 40
F25	311 ± 48
F75	448 ± 94
U30	731 ± 87

inferred from the microstructural and tribological tests. Indeed, a higher emission rate has been recorded for the U30 material (see Table 5). These results confirm further that the recycled friction material is more eligible than underlayer to be used in the recycling process of brake pads, although to a limited extent (25 wt%). A higher friction coefficient leads to a higher emission of wear debris, in agreement with the findings of a PoD study on friction materials for vehicular brakes [25,26]. Interestingly, slightly lower emissions have been recorded for the sample containing recycled friction material only, i.e., the F92P8 sample, still in comparison with the REF sample. The mechanical integrity and tribological performances of friction materials for brake pads greatly depend on the phenolic resin used as a binder [27–29]. The crosslinked structure of the phenolic resin holds all ingredients of the composite together. This lowers the level of emissions although there are some side effects on mechanical properties and a reduction in the stiffness and compressive strength [30,31], as it can be observed in Fig. 9b.

There is a direct correlation between emission rate and the formation of friction layer on the surface of the mating bodies. In the initial stages of the PoD test, the friction layer is progressively built up and is enlarged by the accumulation of the wear particles. These wear particles are produced during the test and compacted to form the so-called secondary plateaus, being the primary ones constituted by the metallic fibers and other tough components of the friction material. The primary plateaus act as barriers to the wear particles, promoting their compaction to form the secondary plateaus. The flux of emitted particles, including the airborne fraction, depends on the dynamic formation and disruption of the secondary plateaus. This mechanism is influenced by the dynamic coupling of the two mating surfaces, pin and disc, and the resulting coefficient of friction. The progressive raise of this parameter, in passing from the running in stage to the steady state one, indicates its direct dependence on the friction layer extension [32]. The characterization of the friction layers obtained for the different materials under different testing conditions is presented in the following section.

3.7. Worn surfaces – SEM analyses

As anticipated, the friction layer is characterized by the presence of primary and secondary plateaus, that can be observed onto the pin and,

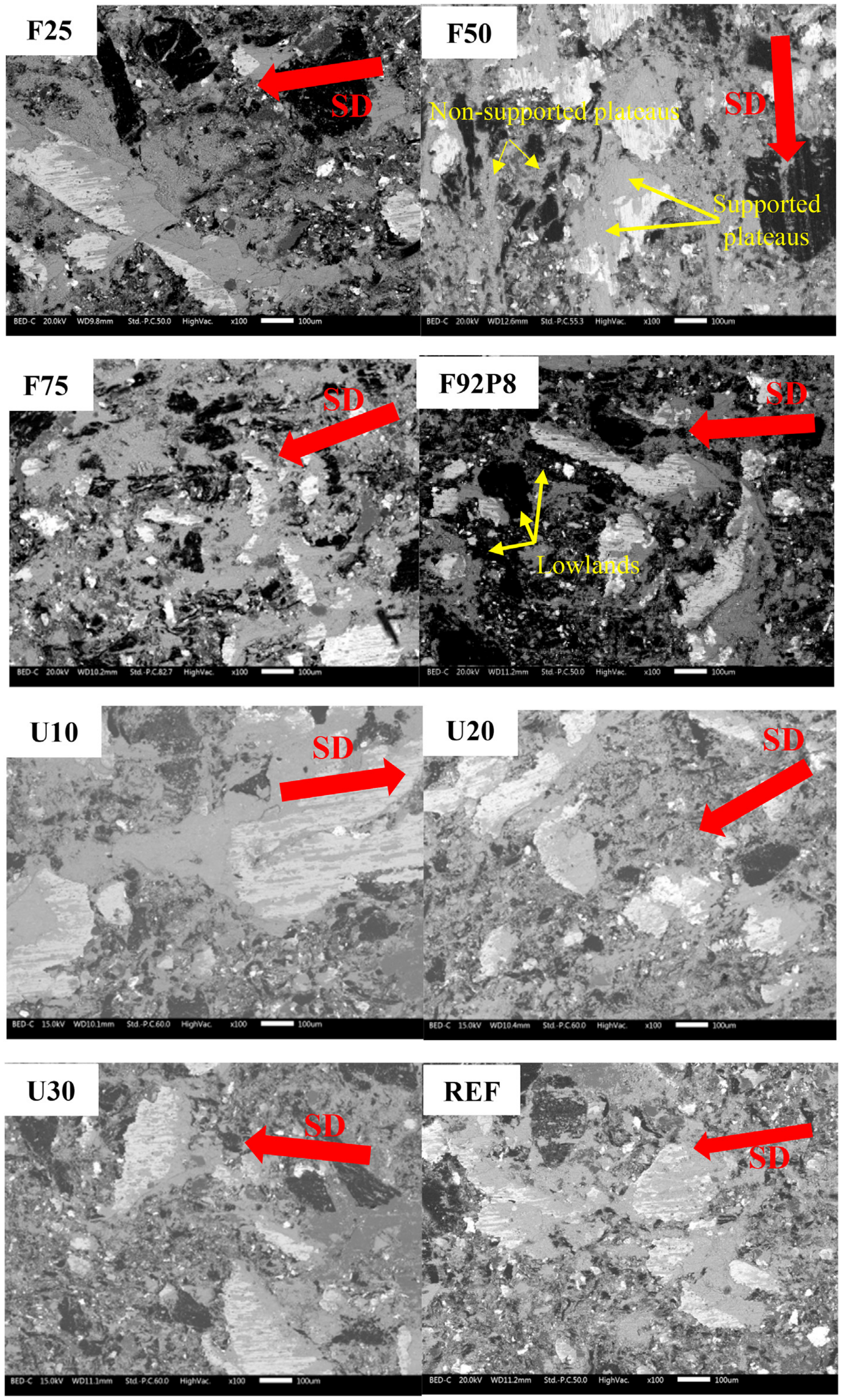


Fig. 12. SEM images of the worn surface of the pins with different compositions, as indicated in each picture.

to some extent, disc surface [12]. Fig. 12 shows the worn surfaces of the pins after the PoD test for all samples. The sliding direction during the wear test is indicated by "SD" in the micrographs. The composite structure of the friction layer is clearly visible. The brighter metallic fibers (primary plateaus) promote the formation of the secondary plateaus, appearing in uniform grey color. It can be seen that the primary plateaus cover approximatively the same surface area for all pins, irrespective of their different formulations. Lowlands covered-area instead are more evident in F92P8 and U-formulations, due to presence of a higher percentage of binder in the initial composition. In U-formulations, however, the secondary plateaus turn out to become smaller as the percentage of underlayer recycled material increases. This confirm the difficulty for the underlayer constituents to form high quality secondary plateaus most probably for some constraint to their compaction due to their internal heterogeneities. There are no signs of sliding contact in lowland areas. According to Eriksson et al. [21], the removal of material from these areas is due to two main reasons: an insufficient compaction pressure of the wear debris trapped between the pin and disc surface; the decomposition and mechanical degradation of the phenolic resin, which releases CO, CO_2 or other gaseous decomposition products. The wear behavior is not an intrinsic material property and it is influenced by the friction conditions of each ingredient present on the sliding surfaces and the contact pressure between pin and disc [33,34].

Some secondary plateaus on the surface of the analyzed worn specimens appear occasionally not supported by any primary plateaus, as indicated in Fig. 12 for sample F50. This type of secondary plateaus, which are generally smaller in size than those supported by a metallic fiber or hard particle, i.e., a genuine primary plateaus, has already been reported in the literature and classified as "Type II", with reference to NAO friction materials [13,35]. Comparing the wear surfaces of F-formulations with the one of REF material, it can be stated that the invariance of the plateaus extension and its high similarity with REF material accounts for the invariance of their tribological properties.

4. Conclusions

This investigation has assessed the feasibility of a recycling procedure for worn out brake pads. The residual friction material and underlayer have been selectively removed from the pad backplate, using an end-milling process. The recycled powder obtained in this way is ready to be added to a virgin masterbatch mix to produce new friction materials having, as demonstrated by PoD tests, similar tribological properties as the reference friction material, taken as benchmark of the present research. The main results obtained in this study can be summarized as follows.

- The hardness of the samples with different percentages of recycled brake pad material remained approximately the same as the reference material, except for the sample F92P8, which showed a slight softening.
- The compressive elastic modulus and strength were comparable to the reference values when introducing into the mix no more than 30 wt% of recycled both underlayer and friction material. Samples with higher percentages of recycled friction materials (F50, F75, and F92P8) showed a declining trend in the compressive properties.
- Owing to the presence of a higher percentage of rubber, the samples containing recycled underlayer exhibited unstable and higher friction coefficient together with a higher specific wear coefficient respect to the reference sample.
- On the other hand, the results for F-formulations, i.e., containing recycled friction material additions, were similar to the results of the reference sample.
- Samples with low percentage of friction materials showed level of emissions slightly higher than the reference sample. Sample F92P8, on the contrary, exhibits a slightly lower emission rate than the reference sample.
- SEM micrographs on the worn surface of the pins evidenced rather similar features of the plateaus, particularly as concerns their extension, in the recycled and reference materials samples.
- Coherently with these observations, a tribological behavior, friction coefficient and wear rate, comparable to the REF material has been detected in the F-samples.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] F. Amato, Non-exhaust Emissions: an Urban Air Quality Problem for Public Health; Impact and Mitigation Measures, Academic Press, 2018.
[2] N. Bukowiecki, et al., PM10 emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland, Atmos. Environ. 44 (19) (2010) 2330–2340.
[3] H.D. van der Gon, J. Hulskotte, A. Visschedijk, M. Schaap, A revised estimate of copper emissions from road transport in UNECE-Europe and its impact on predicted copper concentrations, Atmos. Environ. 41 (38) (2007) 8697–8710.
[4] M. Krzyżanowski, B. Kuna-Dibbert, J. Schneider, Health Effects of Transport-Related Air Pollution, WHO Regional Office Europe, 2005.
[5] U. S. E. P. A. EPA, Copper-free brake initiative [Online]. Available: https://www.epa.gov/npdes/copper-free-brake-initiative, , 2016.
[6] X. Xiao, Y. Yin, J. Bao, L. Lu, X. Feng, Review on the friction and wear of brake materials, Adv. Mech. Eng. 8 (5) (2016).
[7] J. Zhang, H. Matsuura, F. Tsukihashi, Processes for recycling. Treatise on Process Metallurgy, Elsevier, 2014, pp. 1507–1561.
[8] E. P. L. ENV/D/000537, Recycle friction material - pilot realization of the material cycle of friction materials. https://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=search.dspPage&n_proj_id=1299&docType=pdf.
[9] Y. Yang, R. Boom, B. Irion, D.-J. van Heerden, P. Kuiper, H. de Wit, Recycling of composite materials, Chem. Eng. Process: Process Intensification 51 (2012) 53–68.
[10] L. Yezhe, M. Jijie, Å.A. Hedlund, W. Jens, O. Ulf, Recycling of worn out brake pads–impact on tribology and environment, Sci. Rep. 10 (1) (2020).
[11] L.T. Matozo, A. Menetrier, A. Tamagña, Analysis of high damping underlayer materials for brake pads and its effects on NVH performance, in: Proceedings of the 24th Annual Brake Colloquium and Exhibition, 01, 2006, p. 3223. Published October 08, 2006 by SAE International in United States, https://doi.org/10.4271/2006-01-3223.
[12] P.C. Verma, L. Menapace, A. Bonfanti, R. Ciudin, S. Gialanella, G. Straffelini, Braking pad-disc system: wear mechanisms and formation of wear fragments, Wear 322 (2015) 251–258.
[13] C. Menapace, M. Leonardi, G. Perricone, M. Bortolotti, G. Straffelini, S. Gialanella, Pin-on-disc study of brake friction materials with ball-milled nanostructured components, Mater. Des. 115 (2017) 287–298.
[14] G. Straffelini, Friction and Wear: Methodologies for Design and Control, Springer, 2015.
[15] U. Olofsson, L. Olander, A. Jansson, A study of airborne wear particles generated from a sliding contact, J. Tribol. 131 (4) (2009).
[16] M. Leonardi, C. Menapace, V. Matějka, S. Gialanella, G. Straffelini, Pin-on-disc investigation on copper-free friction materials dry sliding against cast iron, Tribol. Int. 119 (2018) 73–81.
[17] A. Belhocine, N.M. Ghazaly, Effects of Young's modulus on disc brake squeal using finite element analysis, Int. J. Acoust. Vib. 21 (3) (2016) 292–300.
[18] M. Makrahy, N. Ghazaly, A. Moaaz, Effect of compressibility of brake friction materials on vibration occurrence, Int. J. Transp. Veh. Eng 11 (2017) 1782–1785.
[19] C.M.R. Ghazali, H. Kamarudin, S.B. Jamaludin, M. Abdullah, Comparative study on thermal, compressive, and wear properties of palm slag brake pad composite with other fillers, in: Advanced Materials Research, vol. 328, Trans Tech Publ, 2011, pp. 1636–1641.
[20] M. Badri, D.S. Arief, A. Prayitno, Compressive strength and wear behavior of palm slag composites using various percentage weight of materials content, Proceedings of Ocean, Mechanical and Aerospace–science and engineering (November) (2015) 1–4.
[21] M. Eriksson, F. Bergman, S. Jacobson, On the nature of tribological contact in automotive brakes, Wear 252 (1–2) (2002) 26–36.
[22] J. Bijwe, Composites as friction materials: recent developments in non-asbestos fiber reinforced friction materials—a review, Polym. Compos. 18 (3) (1997) 378–396.
[23] G. Straffelini, L. Maines, The relationship between wear of semimetallic friction materials and pearlitic cast iron in dry sliding, Wear 307 (1–2) (2013) 75–80.
[24] A.E. Anderson, Friction and Wear of Automotive Brakes, ASM International, 1992.
[25] J. Wahlström, A. Söderberg, L. Olander, A. Jansson, U. Olofsson, A pin-on-disc simulation of airborne wear particles from disc brakes, Wear 268 (5–6) (2010) 763–769.
[26] G. Perricone, et al., A concept for reducing PM10 emissions for car brakes by 50%, Wear 396 (2018) 135–145.
[27] M.H. Cho, S.J. Kim, D. Kim, H. Jang, Effects of ingredients on tribological characteristics of a brake lining: an experimental case study, Wear 258 (11–12) (2005) 1682–1687.
[28] P. Gurunath, J. Bijwe, Friction and wear studies on brake-pad materials based on newly developed resin, Wear 263 (7–12) (2007) 1212–1219.
[29] P. Cai, Y. Wang, T. Wang, Q. Wang, Effect of resins on thermal, mechanical and tribological properties of friction materials, Tribol. Int. 87 (2015) 1–10.
[30] D.C. Jara, H. Jang, Synergistic effects of the ingredients of brake friction materials on friction and wear: a case study on phenolic resin and potassium titanate, Wear 430 (2019) 222–232.

[31] M. Shin, J. Kim, B. Joo, H. Jang, Wear and friction-induced vibration of brake friction materials with different weight average molar mass phenolic resins, Tribol. Lett. 58 (1) (2015) 10.

[32] A.P. Nogueira, M. Leonardi, G. Straffelini, S. Gialanella, Sliding behavior and particle emissions of Cu-free friction materials with different content of phenolic resin, Tribol. Trans. (2020) 1–12.

[33] J. Wahlström, L. Olander, U. Olofsson, A pin-on-disc study focusing on how different load levels affect the concentration and size distribution of airborne wear particles from the disc brake materials, Tribol. Lett. 46 (2) (2012) 195–204.

[34] H. Jang, K. Ko, S. Kim, R. Basch, J. Fash, The effect of metal fibers on the friction performance of automotive brake friction materials, Wear 256 (3–4) (2004) 406–414.

[35] P. Neis, N. Ferreira, G. Fekete, L. Matozo, D. Masotti, Towards a better understanding of the structures existing on the surface of brake pads, Tribol. Int. 105 (2017) 135–147.