

Efforts towards green friction materials

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ABSTRACT

Copper is an outstanding ingredient of friction materials (FMs) due to its multi-functional performance. Despite all its various positive contributions in FMs, it has been recently reported as a hazard for an aquatic life and has become a focus of concern for the FM Industry.

Hence in the current work, group of novel ingredients was explored for Cu-replacement. Some conducting ingredients were added to compensate the conductivity of Cu. One more novel ingredient Promaxon-D was used as a theme ingredient.

The developed pads (metal-free) were characterized for tribological properties on the inertia dynamometer as per JASO-C-406 standards. It was concluded that Promaxon-D proved successful in Cu-replacement almost in all respects barring wear. With increase in an amount of Promaxon-D, most of the properties got improved.

1. Introduction

Generally, non-asbestos organic (NAO) friction materials (FMs) contain more than 10–20 ingredients to satisfy the conflicting performance requirements such as moderate and stable friction, resistance to fade, wear, squeal, noise and good recovery of friction, etc. Every ingredient added to the FMs has some specific functions to perform and hence accordingly they are classified under four main subgroups like binder resin, reinforcing fibers, friction modifiers, and functional fillers as shown in Table 1.

It is necessary that the ingredients used should be environment friendly. For example, asbestos, although had unparalleled performance properties, was discarded because of its hazardous effects on the human life. Copper (Cu) is an outstanding ingredient due to its multi-functionality such as high thermal conductivity (TC) which is beneficial to dissipate the large amount of heat generated during the braking action; offering structural integrity to the composites, acts as a lubricant at high temperature and compensates for the increased abrasivity of graphite at high temperature and helps in stable transfer film formation, which in turn, reduces the fluctuations in friction [1–3]. Despite all these positive aspects of Cu, some indirect adverse effects on the environment are recently reported. Increased contribution of non-exhaust emissions due to vehicular traffic pollution has become a major threat to the environment including human, animals etc. [4]. According to the study carried out by various researchers, (shown in Table 2), [5–10] Cu is the major part of brake wear debris and proved as a fresh water

pollutant in the urban areas [11,12], which threatens the aquatic life and has become a focus of concern for the FM Industry. The literature survey [10,13–18] on the harmful effects of metallic ingredients used in FMs on living organisms and environment is given in Table 3.

Thus, considering all these harmful effects of Cu on living organisms and environment, it becomes utmost important to replace it from FMs [19]. As per new environmental regulations, the USA has signed the legislation to restrict the use of Cu in brake-pads [20] shown in Table 4.

Cu replacement has become extremely difficult task due its unique and multi-functional performance in FMs and worldwide extensive research is going on for removal of Cu by finding the right substitute/s. Researchers tried various ingredients for Cu substitution, without full success. Available literature indicates that no single material can substitute Cu due to its multi-functionality. The literature efforts for Cu substitution are compiled in Table 5 and broadly categorized as solid lubricants [20–23], different metals [24–27], organic fibers [28–31] and inorganic fillers [32].

Keeping the efforts in open literature in view, it was thought of developing metal-free NAO brake-pads, which could be similar or better in performance with Copper containing brake-pads. Literature also showed that achieving equal wear resistance in Cu-free FMs is quite difficult. It was also realised that no single ingredient can compete copper. Hence in the current work, group of novel ingredients was explored for Cu-replacement. To compensate the TC of Cu, more thermally conducting rockwool fibers (RB205) and special graphite (C-THERM™011 and Timrex PC40) were chosen.

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Nomenclature		WS ₂	Tungsten disulfide
NAO	Non-asbestos organic	SnS ₂	Tin disulfide
FM	Friction material	Special iron alloy	SIA
CNSL	Cashew nut shell liquid	SL	Solid lubricant
Cu	Copper	Al	Aluminum
TC	Thermal conductivity	SSS	Stainless steel swarf
BPWD	Brake-pad wear debris	Sb	Antimony
MOORA	Multiple objective optimization on the basis of ratio analysis	μ	Coefficient of friction
h-BN	Hexagonal boron nitride	EDAX	Energy Dispersive X Ray Spectroscopy
W _R	Wear resistance	PAN	Polyacrylonitrile
F _R	Fade resistance	SEM	Scanning electron microscope
		F&R	Fade and recovery

One more novel ingredient Promaxon-D – which is a synthetic hydrated calcium silicate with a chemical structure similar to the mineral Xonotlite Ca₆Si₆O₁₇ (OH)₂ was used as a theme ingredient. It is a very stable material with high heat resistance and low TC. Also, it has special spherical morphology with micro-pores inside and outside. Hence it was also used with a view that it would add improvement in fade resistance (F_R) by sustaining at high temperatures. Since there is no literature available on its optimized amount and its effect on performance parameters, three FMs in the form of brake-pads were developed by keeping identical parent composition and varying the Promaxon-D

amount 0 wt% (P₀), 5 wt% (P₅) and 10 wt% (P₁₀). One more composite (C₁₀) was developed with 10 wt% Cu and without Promaxon-D and other ingredients with lower TC for the sake of comparison. These composites were evaluated for density, porosity, hardness, uncured resin content and tribo-performance on full scale inertia dynamometer by following JASO C 406 testing standard. Overall performance ranking of composites was done by MOORA (Multiple objective optimization on the basis of ratio analysis) method. The details are discussed in the subsequent sections.

Table 1
Classification of ingredients used in FMs.

Class	Function	Ingredients
Binder	Firmly binds ingredients together	Straight phenolic resins and their modified forms such as cashew nut shell liquid (CNSL) resins, elastomer modified resins, cresylic resins etc.
Fibers	Improve mechanical strength and integrity, thermal stability (depending on the fiber type) friction and wear properties	Glass, steel, aramid, carbon, rock-wool, polyacrylonitrile, basalt, cellulose etc.
Friction modifiers	Impart desired friction characteristics	Al ₂ O ₃ , SiO ₂ , ZrO ₂ , Cr ₂ O ₃ etc. Graphite, MoS ₂ , Sb ₂ S ₃ etc.
Fillers	Space fillers to cut the cost and functional fillers to improve the specific properties	Space filler-BaSO ₄ , CaCO ₃ etc. Functional filler- Copper, brass, iron, aluminum, vermiculite, wollastonite, cashew dust, potassium titanate etc.

Table 2
Literature on brake-pad wear debris-(BPWD).

Brief contents	Ref.
BPWD consists of the elements Cu, Fe and Ba in both dynamometer and test track samples. 50% of pad- wear produce airborne debris which led to env. pollution and adversely affects human health.sss	[5]
Brake-pads - major contributors to Cu- pollution of bay water.	[6]
Out of 2.6 × 10 ³ ton/year of total European Cu emission, 2.4 × 10 ³ ton/year Cu emission was due to BPWD.	[7]
Emitted airborne Cu particles from BPWD deposit on the ground and then reaches into rivers, bays, marine waters etc.	[8]
Sources of Pb, Cu, Cd and Zn in urban storm water runoff - major source is BPWD.	[9]
Motor vehicles are key sources of toxic pollutants like Cu and heavy metals from the exhaust and brake wear.	[10]

Table 3
Harmful effects of metal debris on the health and environment.

Element of study	Effect of the corresponding element on living organisms and environment	Ref.
Cu	Cu polluted water has the potential to cause chemosensory deprivation and increased predation mortality in exposed salmon. Adversely affects the olfactory system of fishes	[10,13]
Cu, Hg	Adversely affects the olfactory response of <i>Salmo gairdneri</i>	[14]
Cu	Causes gastrointestinal distress, irritation to the respiratory tract, acute Cu poisoning may lead to liver injury and kidney failure in humans.	[15]
Fe, Cu, Mn	May damage the lung cells tight junctions by oxidative stress in humans.	[16]
Sb	Affects eye, skin and respiratory system and causes inflammation of the lungs, chronic emphysema and chronic bronchitis in humans.	[16]
Fe	May cause conjunctivitis, retinitis and choroiditis and enhances the risk of lung cancer of humans.	[17]
Cu, Fe	Brake wear debris has a direct adverse effect on water quality	[18]

Table 4
Legislations for restricting use of Cu in brake-pads.

Restricted materials	Deadline	Legislations signing states
No asbestos, Chromium, Mercury, Cadmium, Lead	2014	Washington, California
Less than 5 wt% Cu	2021	Washington, California, Rhode, Island, Oregon
Less than 0.5 wt % Cu	2023	Washington
Less than 0.5 wt % Cu	2025	California

2. Materials and methodology

Details of all ingredients used in the brake-pad development are given in Table 6. Technical specifications of theme ingredients viz. Promaxon-D and Cu are given in Table 7.

Fig. 1 confirms the morphology of Promaxon-D. Fig. 1 (b) shows Promaxon-D particle looking like a spherical ball. Close view Fig. 1 (c) of outer surface of spherical ball shows knitted needle-like crystal structure. Inside view of Promaxon-D particle in Fig. 1 (d) is a porous

Table 5
Literature efforts for Cu replacement in FMs.

Materials used for Cu replacement	Brief contents	Ref.
Various types of graphites	Combination of primary synthetic TIMREX [®] T graphite with C-THERM [™] 011 graphite gives the best results in terms of heat dissipation and NVH performance.	20
Thermo-graphite	Though it increased TC, it also affected the friction and wear properties and reduced fade.	21
Hexagonal boron nitride (h-BN)	hBN can be a choice in Cu-free brake pads but showed lower wear resistance (W_R).	22
Graphite, Sb_2S_3 , and MoS_2	FMs containing Sb_2S_3 + graphite enhanced friction stability and fade resistance (F_R) but Sb belongs to harmful ingredients	23
Fe and Special iron alloy (SIA)	Investigated the effect of Cu, Fe and special iron alloy with a combination of special fibres and two common metal sulphides as SLs in Cu-free low steel brakes and claimed for successful replacement for Cu.	24
Steel and Al fibers	Investigated the effect of Cu, steel and Al fibers on tribo-performance of FMs and concluded that Al fibres showed the possibility of friction layer formation and showed lowest specific wear rate while steel fibers showed highest wear.	25
steel fibers	Cu containing FMs supported compact and adherent secondary plateaus formation while FM without Cu showed highest wear and lowest μ .	26
stainless steel swarf (SSS)	Almost all the performance parameters of stainless-steel containing pads were better than Cu containing pads confirming that SSS can be the appropriate replacement for Cu in brake pads at the cost of wear.	27
Jute fibers and powdered hazelnut shells	Not sustaining high braking temperature and also showing high wear rate.	28
Geo-polymer, hemp and Kevlar fibers	Cu and Sb-free pads outperformed in fade section but showed higher wear rate than Cu and Sb based pads	29
Sisal fibers	Showed high μ and W_R up to 250 °C	30
Natural fibers	enhanced friction stability and high F_R at the cost of recovery performance	31
Barite	Basic possibility of Cu replacement by barite was tried and evaluated on pin-on-disc machine. Large amount of barite particles was found in wear debris which prevented friction layer formation.	32

Table 6
Details of ingredients used in the brake-pads.

Ingredients	Size of particles	Source details of ingredients
Parent ingredients		
Phenolic resin	74 μ m	Local Supplier.
Friction dust	150 μ m	Satya Cashew Chemicals, Chennai, India.
Rockwool RB-205	L.-150 \pm 25 μ m; D.-5.5 μ m	Lapinus Fibers, Netherlands.
Rockwool RB-250	L.-125 \pm 25 μ m; D.-5.5 μ m	Lapinus Fibers, Netherlands.
Twaron pulp 1099	L.-1.35 mm; D.-12 μ m	Teijin Aramid, Netherlands.
PAN fiber-CFF 110-1	D.-10 μ m	Sterling Fibers Inc. USA.
C-THERM [™] 011	20-50 μ m	Imerys Graphite & Carbon, Switzerland.
Timrex PC40	40 μ m	Imerys Graphite & Carbon, Switzerland.
Alumina	48-100 μ m	Hindalco Industries, Delhi, India.
Potassium Titanate	15-25 μ m	Otsuka Chemicals Co., Ltd. USA.
Glass fiber	L.-3-6 mm	} Starke International Ltd., Delhi, India.
Vermiculite	100-350 μ m	
Natural Graphite	100-200 μ m	
Barite	10-100 μ m	
Theme ingredients		
Promaxon-D	35 -85 μ m	Promat International N.V. Belgium.
Copper	280-430 μ m	Kandoi Metals, Jaipur, India.

Table 7
Specifications of theme ingredients [Suppliers' data].

Properties	Promaxon-D	Copper
Appearance	Powder	Powder
Avg. Particle Size	35–85 μ m	280–430 μ m
True Density (g/cm^3)	2.6	8.96
Melting Point ($^{\circ}C$)	1540	1085

net like structure. The EDAX images (dot mapping of Ca, Si and O) of Promaxon-D are shown in Fig. 2. Details of Rockwool and graphite are given in Tables 8 and 9.

2.1. Design and development of brake-pads

Three brake-pads were developed with 75 wt % parent composition with more thermally conducting ingredients and 25 wt % theme ingredients. In these three brake-pads amount of Promaxon-D was varied by 0, 5 and 10 wt % and the remaining amount was compensated by

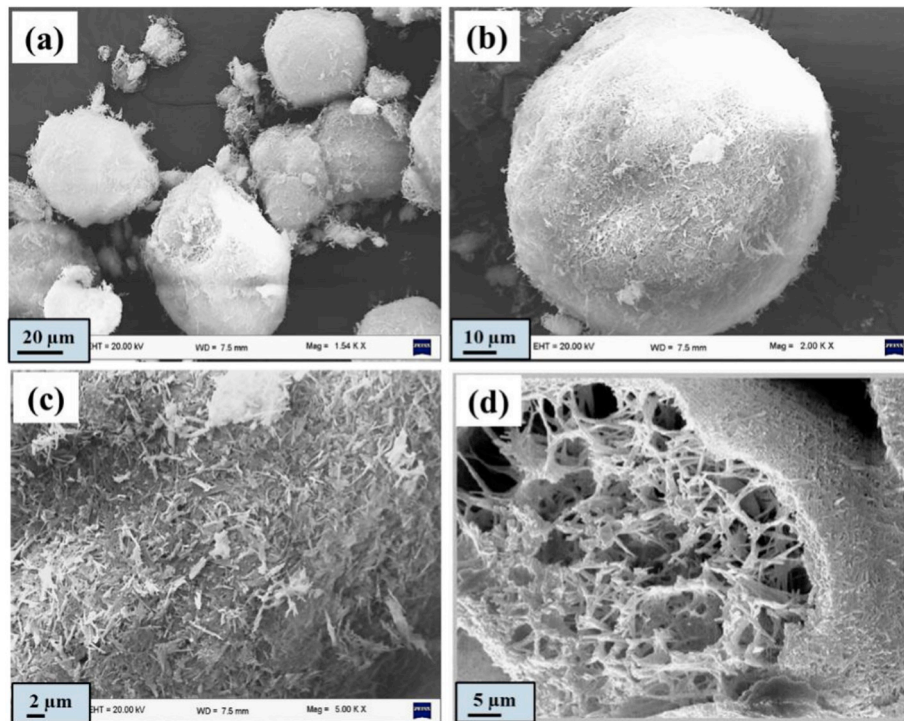


Fig. 1. (a–b) SEM micrographs of Promaxon-D particles (c) outer surface and (d) inner structure of Promaxon-D particle.

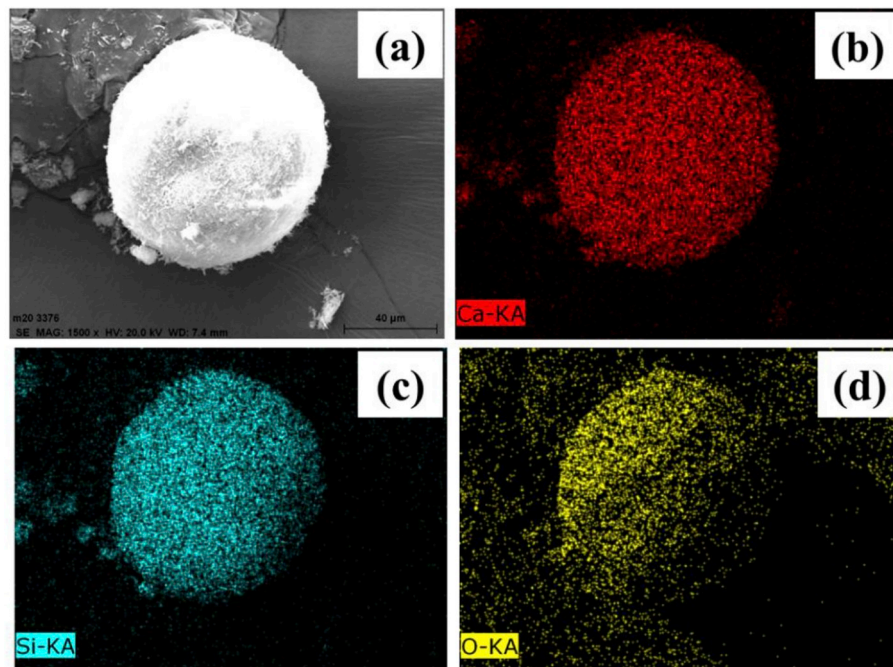


Fig. 2. (a) SEM and (b–d) EDAX of Promaxon-D particles (dot mapping for Ca, Si and O).

inert filler barite. These brake-pads were designated as P₀, P₅ and P₁₀ depending on content of Promaxon-D. For comparison purpose one more brake-pad containing Cu and less conducting ingredients was developed and designated as C₁₀. Table 10 shows the compositions and designations of all brake-pads.

Brake-pads were prepared as per industrial standards already discussed in earlier papers [33–35]. Ingredients were mixed in a plough shear mixer for 22 min as shown in Table 11. After homogeneous mixing composites were cured at 160 °C and 140 bar pressure for 9 min as per details published earlier [33–35].

Table 8
Specifications of Rockwool fibres.

Property Details	Rockwool (RB250)	Conducting Rockwool (RB205)
Commercial name	Rock brake RB250; Roxul 1000	Rock brake RB205; Roxul 1000
Specific density	2.75 ± 0.15 g/cm ³	2.6 ± 0.25 g/cm ³
Color	Grey/green	Black
Thermal conductivity	0.037 W·m ⁻¹ ·K ⁻¹	1.22 W·m ⁻¹ ·K ⁻¹
Non-fibrous material	< 1 wt%	0.08–0.2 wt%

Table 9
Specifications of graphites.

Property Details	Natural Graphite	C-THERM™ 011
Ash	12.6%	1.29%
Bulk density	0.38 g/cm ³	0.15 g/cm ³
Real density	2.25 g/cm ³	2.24 g/cm ³
Specific surface area (BET)	3.3 m ² /g	24.3 m ² /g

Table 10
Formulations and designations of brake-pads.

Ingredients by wt.%	Designations of FMs			
	P ₀	P ₅	P ₁₀	C ₁₀
Parent Composition ^a	55	55	55	55
Rockwool RB-205	10	10	10	–
Rockwool RB-250 C-THERM™011 (graphite with higher TC)	–	–	–	10
Timrex PC40 (coke)	5	5	5	–
Natural graphite	–	–	–	10
Pormaxon-D	0	5	10	–
Copper	–	–	–	10
Barite	25	20	15	15

^a Parent composition - binder: fibers: abrasives: functional fillers - 10:11:2:32

Table 11
Mixing schedule of ingredients in plough shear mixture.

Ingredients	Mixing duration (minutes)
Aramid pulp and glass Fibers	1
Aramid-glass fibers mixture + Barite	5
Previous + RB205 + PAN (Batch-I)	10
Promaxon-D + Remaining all powdery ingredients (Batch-II)	4
(Batch I) + (Batch-II)	2
Total Duration	22 min

Table 12
Data on physical, chemical and mechanical characterization.

Properties	P ₀	P ₅	P ₁₀	C ₁₀
Density (g/cc)	1.95	1.71	1.57	2.08
Oil porosity (%) (JIS D 4418)	1.38	2.34	3.52	1.88
Water porosity (%) (JIS D 4418)	2.96	3.5	3.89	2.56
Acetone extraction (%) (ASTM D 494)	0.17	0.14	0.13	0.12
Thermal conductivity (TC)	1.07	1.00	0.72	0.96
Hardness (HRS) (ASTM D 785)	96	93	95	101

2.2. Characterization of brake-pads

The developed pads were characterized for density, oil and water porosity, acetone extraction, thermal conductivity (TC) and hardness as per standards mentioned in Table 11.

2.3. Testing on full scale brake dynamometer for performance evaluation

Pads were evaluated for tribo-performance on full scale brake inertia dynamometer as per (JASO C406) schedule and the details of testing, schematic diagram of dynamometer, technical specifications and working description were explained in the earlier literature [36,37].

3. Results and discussions

The results of physical, chemical and mechanical characterization of the pads as well as tribological performance evaluation are discussed in the following sections. Wear mechanisms are explained with the help of SEM micrographs of worn surfaces of pads and discs. Finally, performance ranking was done using MOORA method.

3.1. Characterization of the brake-pads

The results of density, oil and water porosity, acetone extraction, TC and hardness of composites are shown in Table 12 (average value of three trials carried out for each test was considered).

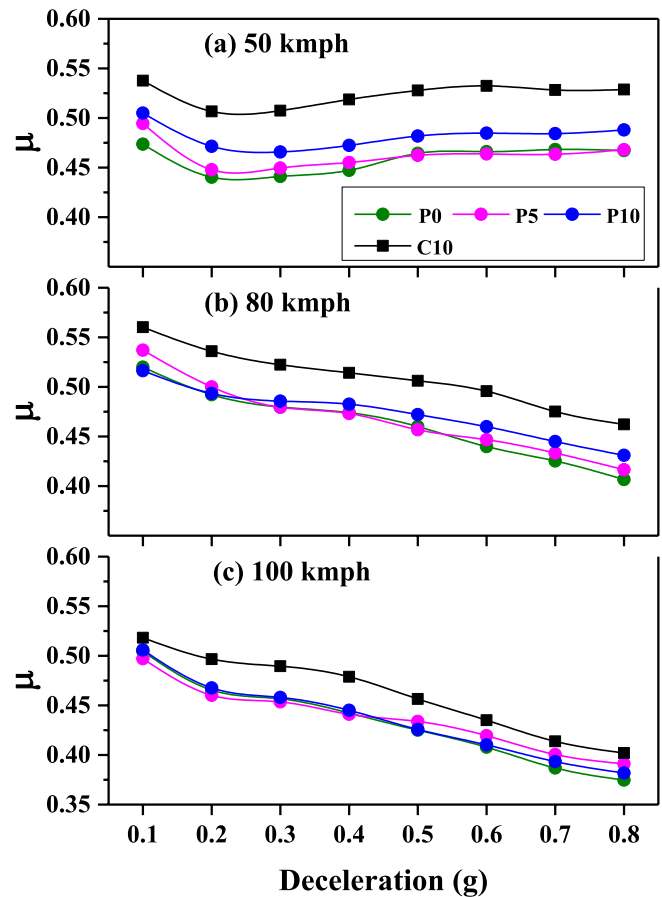


Fig. 3. Sensitivity of μ towards pressure at (a) 50 kmph, (b) 80 kmph and (c) 100 kmph.

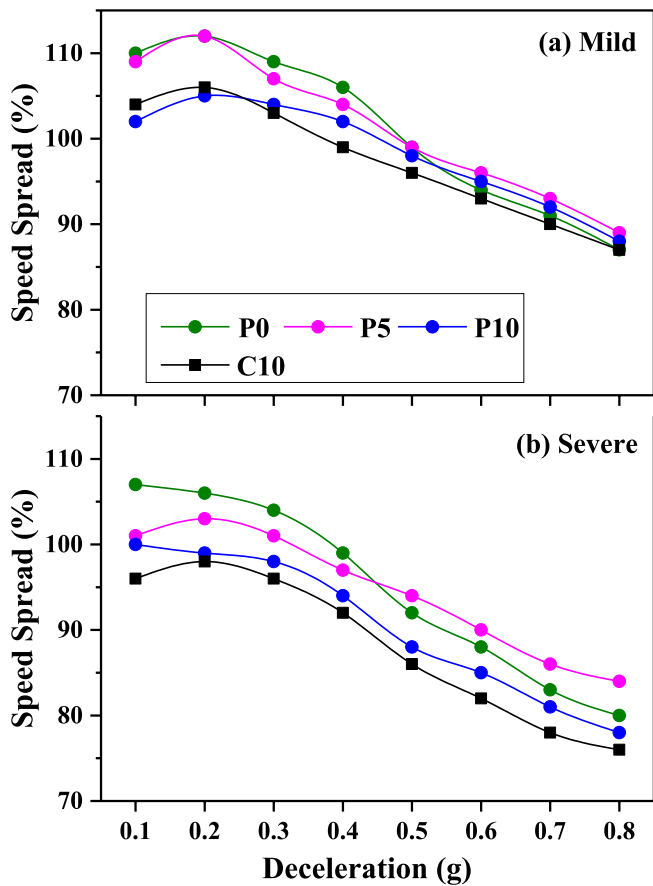


Fig. 4. Sensitivity of μ towards speed at mild and severe conditions.

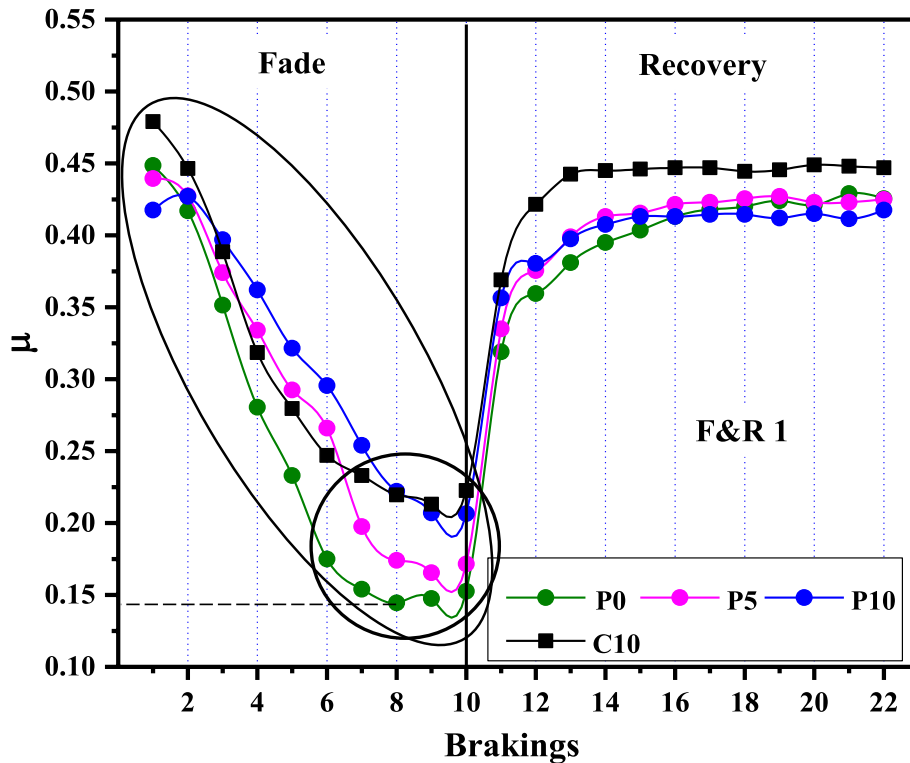


Fig. 5. Sensitivity of μ for temperature for F&R I.

Density results showed decrease with an increment in Promaxon-D content. This can be correlated to the replacement of heavier material by a lighter one. Amongst all, C₁₀ showed highest density. Porosity showed opposite trends. Uncured resin percentage got reduced with inclusion of Promaxon-D indicating possibility of catalysing the curing process. TC showed decreasing trend with increase in Promaxon-D content. This can be correlated to the inclusion of Promaxon-D, a low conducting ingredient than barite. C₁₀ showed higher TC than P₁₀. Hardness was not affected appreciably due to Promaxon-D. C₁₀ showed highest hardness.

3.2. Tribological behaviour of the brake-pads on dynamometer testing

Each Brake-pad was evaluated two times for tribological performance on a brake inertia dynamometer as per JASO C406 standard schedule and average of two values was reported. Every time fresh disc and pair of pads were used. Results of sensitivity of friction performance towards pressure and speed are shown in Figs. 3 and 4 respectively. Figs. 5–9 show results and essence of μ sensitivity towards temperature for fade and recovery (F&R) cycles I and II. SEM micrographs of worn surfaces are shown in Figs. 10–12. Finally, FMs were ranked for their performance by MOORA method and represented by Tables 12 and 13.

3.2.1. Sensitivity of μ towards pressure

Fig. 3 shows the sensitivity of μ towards pressure at three different speeds 50, 80 and 100 kmph. Ideally this graph should be perfectly straight and parallel to the X-axis with least undulations. Decrease in friction coefficient with increase in pressure and speed are generally referred as pressure fade and speed fade respectively. Results from Fig. 3 show that overall μ range was 0.37–0.57 for all brake-pads and there was a slight decrease in μ with pressure at higher speeds. Pressure fade i.e. decline in the μ with pressure (deceleration in this case) mainly

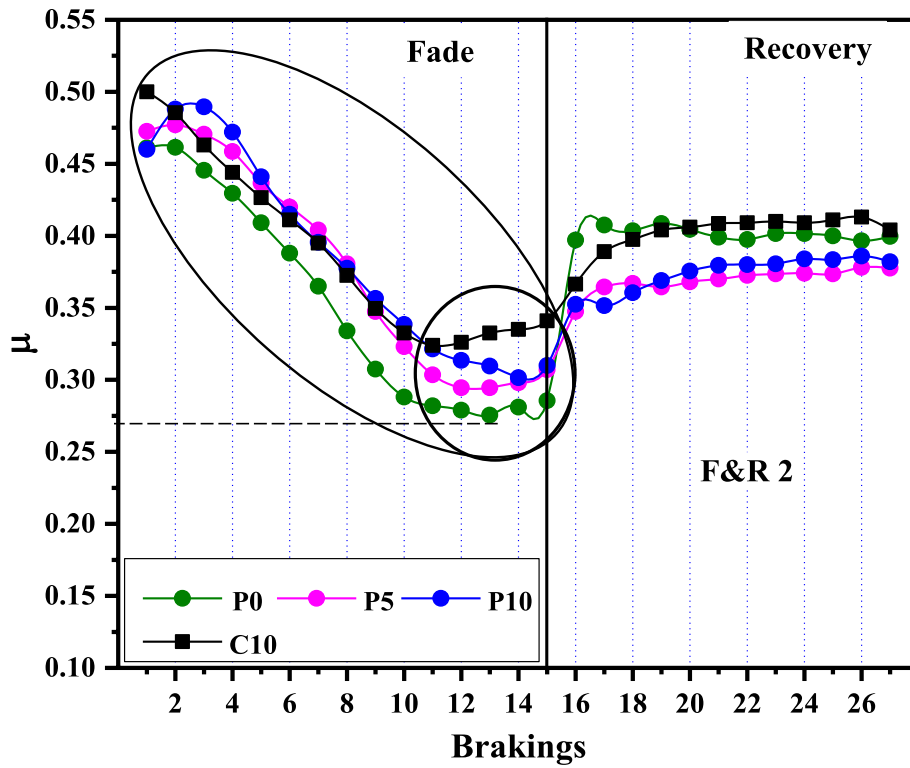


Fig. 6. Sensitivity of μ for temperature for F&R II.

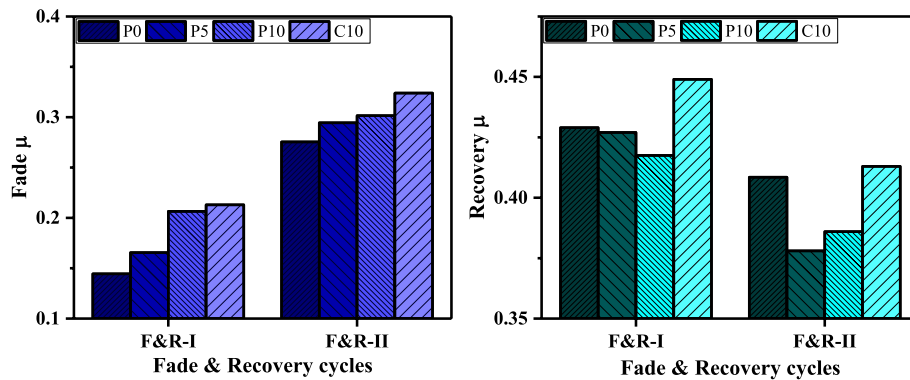


Fig. 7. Fade and recovery μ for F&R I and II.

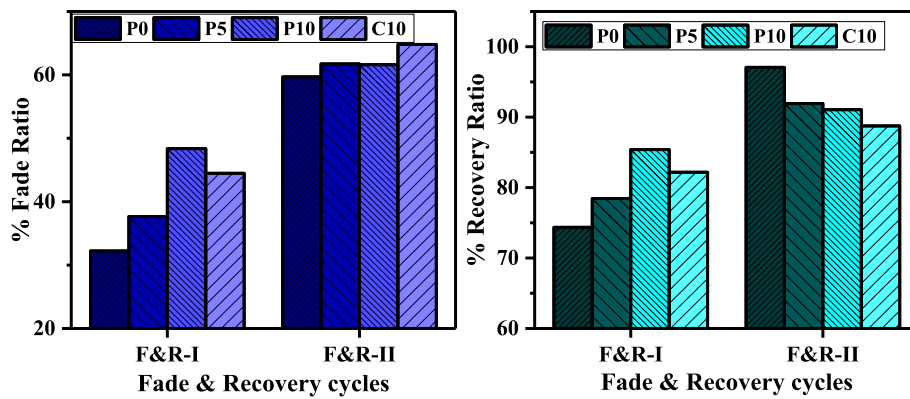


Fig. 8. % Fade and recovery ratio for F&R I and II.

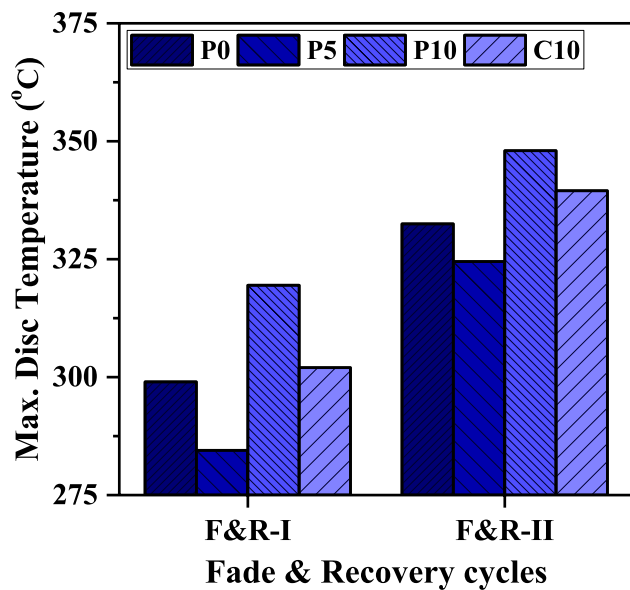


Fig. 9. Disc temperature rise for F&R I and II.

depended on the composition and speed. It was minimum for 80 kmph and highest at highest speed (100 kmph). It was not observed at the lowest speed (50 kmph). Pressure fade sensitivity was speed specific also. It was higher at higher speed.

For polymers and composites Amonton's laws do not hold good and hence μ is not constant when pressure or speed is changed. With increase in severity of speed and other operating conditions, large amount of frictional heat is generated during braking, which leads to the degradation of organic matter. This is the genesis of formation of primary and secondary plateaus. This glazed material has lower μ and hence leads to the fade phenomenon.

When Promaxon-D was added, μ increased slightly because Promaxon-D, a synthetic hydrated calcium silicate, is a mild abrasive with the knitted needle-like crystal structure. This morphology helps in

cleaning glaze and rejuvenating friction performance.

The C₁₀ showed highest μ in the series under all conditions. It was interesting to note that when magnitude of μ of P₀ (25% barite) and C₁₀ (10% Cu and 15% barite) was compared, the μ of C₁₀ was much higher indicating Cu increases μ compared to the barite. In fact, it increases μ compared to Promaxon-D also under all conditions.

3.2.2. Sensitivity of μ towards speed

Sensitivity of μ towards speed for mild and severe conditions is shown in Fig. 4. It was represented in terms of speed spread percentage, which is a percentage ratio of friction performance at higher speed to a lower speed. Mild and severe conditions are referred to the transition from 50 to 80 kmph and 50–100 kmph respectively. Ideally, speed spread should be higher with least undulations for a good quality brake-pad. Results showed that C₁₀ showed lowest performance (highest sensitivity of μ towards speed) and inclusion of Promaxon-D also showed slight deterioration compared to P₀ at lower deceleration values. Otherwise inclusion of Promaxon-D proved beneficial.

3.2.3. Sensitivity of μ towards temperature

Generally, μ sensitivity of FMs towards temperature is represented in terms of fade and recovery performance. Fade is related to the deterioration in μ at elevated temperatures and regaining of original performance at normal conditions is referred as a recovery. Results of μ sensitivity towards temperature in F&R cycle I and II are plotted in Figs. 5–9. Results in Fig. 5 showed improvement in F_R with the inclusion of Promaxon-D. Higher the Promaxon-D contents, higher was the F_R which is beneficial feature. It has a high temperature resistance and shows slight dehydration between 620 °C and 750 °C due to loss of crystalline water without any significant physical changes [38]. It acts as a temporary heat sink and saves.

Surrounding ingredients from degradation leading to increase in F_R. Results in Figs. 5 and 6 (F& R cycles 1 and 2) show that P₀ and P₅ showed highest slopes in general. P₁₀ and C₁₀ showed comparable features. The extracts from these data are shown in Figs. 7 and 8. Fig. 7 shows magnitude of μ (fade and recovery) for the brake-pads. Generally higher the μ , better is the rating of a material. Inclusion of Promaxon D proved beneficial in this respect, although C₁₀ showed highest μ . However, these are not true reflections of material. In general, if the original μ is high, fade μ tends to be high. Best way of comparison is %

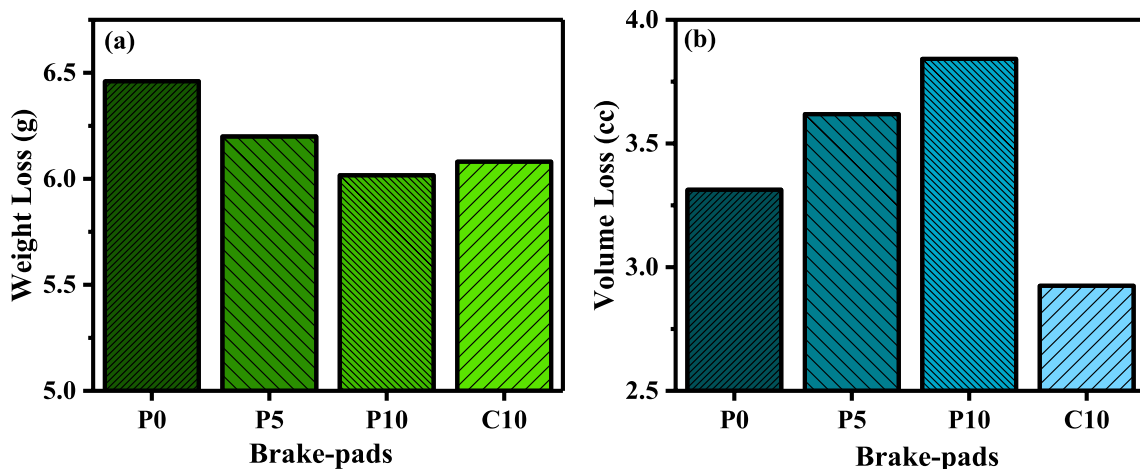


Fig. 10. Wear behaviour of brake-pads (a) Weight loss (b) Volume loss.

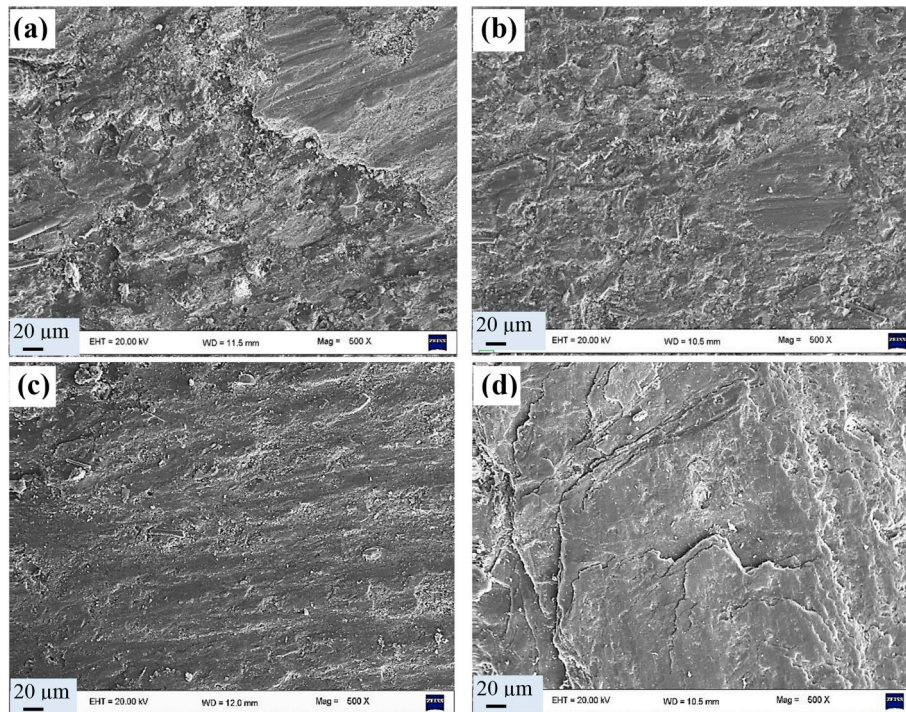


Fig. 11. SEM micrographs of worn surfaces of pads-(a) P₀ (b) P₅ (c) P₁₀ (d) C₁₀.

fade ratio as shown in Fig. 8. P₁₀ almost outperformed C₁₀ (barring Fade ratio in Cycle II) in both fade and recovery characteristics proving successful replacement of Cu in FMs. As the amount of Promaxon D increased, performance also increased.

Fig. 9 shows rise in disc temperature during braking called counter-face friendliness of FMs. Rise in disc temp and front of pad temperature should be as small as possible. One of the major factors responsible for the rise in the disc temperature is the μ itself. Higher the μ , higher will be frictional heat generation and rise in the temperature of disc and pad. Other factors such as TC and thermal diffusivity of pads, temperature of environment etc. also affect this property. P₅ proved best amongst all for lowest rise in disc temperature.

3.2.4. Studies on the wear behaviour of brake-pads

Wear was measured by a weight loss method after completing JASO C406 test. Fig. 10 shows the average wear results of two trials. With an inclusion of Promaxon-D weight loss reduced but wear vol. increased. C₁₀ proved best in wear performance followed by P₀ (Fig. 10 b). Inclusion of Promaxon D led to increase in wear, which was not a positive feature.

3.2.5. Worn surface analysis

Figs. 11 and 12 show SEM micrographs of worn surfaces of brake-pads and rotor discs respectively. Fig. 11 showed that best performing pads had lot of secondary plateaus mainly because of back transfer from the disc. The disc surface against P₁₀ showed very thin and smooth film without cracks.

3.3. Performance ranking of composites by MOORA method

Ranking of brake-pads from best to worst on the basis of their tribological performance was done using MOORA method based on combination of several conflicting performance criteria. The response matrix for MOORA application is shown in Table 13. It consists of four brake-pads as an alternative and six various criteria viz. average μ at moderate speed, fade and recovery ratios in first F&R cycle, friction fluctuations at moderate speed, wear volume and disc temperature.

The detailed application procedure of MOORA method is already discussed in our earlier publications [35,39]. Ranking was done based on normalized assessment shown in Table 14. Higher value of normalized assessment indicates the best performing brake-pad. Results showed that the C₁₀ proved best amongst all brake-pads and P₁₀ proved second best followed by P₅ and P₀.

4. Conclusions

Based on the performance evaluation of brake-pads developed with increasing contents of Promaxon D with a view to replace copper in brake-pad formulation, following conclusions were drawn.

The friction coefficient increased with the inclusion of Promaxon-D particles indicating its slight abrasive nature. Higher the contents, higher was the μ . Promaxon-D also resulted into reducing the sensitivity of μ towards speed and pressure. 5% amount proved most beneficial for low speed sensitivity. Promaxon-D also acted as an anti-fade agent which was very beneficial feature. Higher the amount, less was the fade.

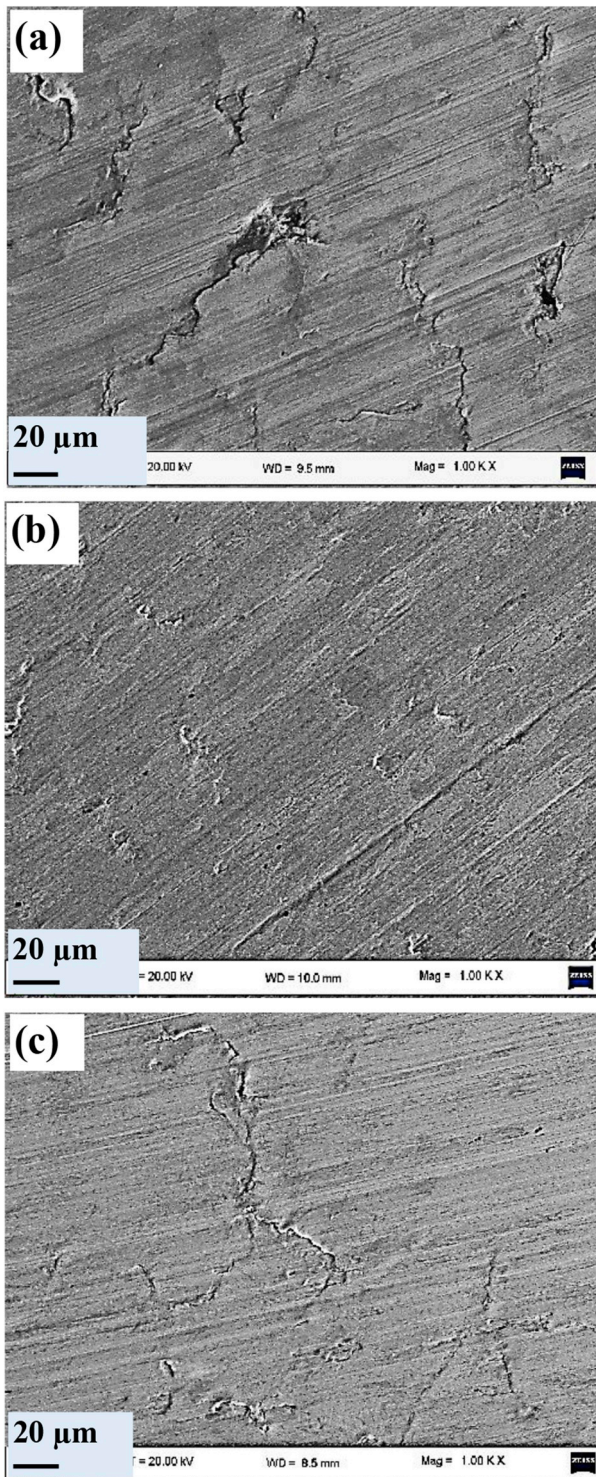


Fig. 12. SEM micrographs of worn discs - (a) P₀ (b) P₁₀ and (c) C₁₀.

When the performance of series of metal-free pads with Promaxon was compared with that with Cu-containing pads, it was concluded that the Cu containing pad exhibited highest μ and wear resistance but proved poorest in μ -speed sensitivity and recovery aspects. Pads with Promaxon D, on the other hand, outperformed Cu-pads almost in all

Table 13
Response matrix for MOORA method.

Criteria	Brake-pads	P ₀	P ₅	P ₁₀	C ₁₀
Avg. μ_{80}		0.462	0.468	0.473	0.509
% Fade ratio 1		32.2	37.7	48.4	44.5
% Recovery ratio 1		74.4	78.5	85.4	82.2
$\Delta\mu_{80}$		0.113	0.121	0.085	0.098
Wear Vol. (cc)		3.31	3.62	3.84	2.92
Disc Temp. (°C)		299	285	320	302

Table 14
Composites ranking for their performance.

Brake-pads	P ₀	P ₅	P ₁₀	C ₁₀
Normalized assessment	-0.177	-0.135	0.121	0.193
Performance ranking	4	3	2	1

respects barring wear. It proved as anti-fade agent. Hence Promaxon-D along with some conducting ingredients can be declared as a successful replacement for Cu.

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References

- [1] Kumar M, Bijwe J. NAO friction materials with various metal powders: tribological evaluation on full-scale inertia dynamometer. *Wear* 2010;269(11):826–37.
- [2] Sterle W, Prielzel C, Kloß H, Dmitriev AI. On the role of copper in brake friction materials. *Tribol Int* 2010;43(12):2317–26.
- [3] Kim SJ, Lee JY, Han JM, Kim YC, Park HD, Sung SH, et al. The role of copper on the friction and wear performance of automotive brake friction materials. *SAE Int J Mater Manuf* 2011;5(1):9–18.
- [4] Amato F, Cassee FR, Denier HA, van der Gon, Gehrig R, Gustafsson M, et al. Urban air quality: the challenge of traffic non-exhaust emissions. *J Hazard Mater* 2014;275:31–6.
- [5] Sanders PG, Xu N, Dalka M T, Maricic MM. Airborne brake wear debris: size distributions, composition, and a comparison of dynamometer and vehicle tests. *Environ Sci Technol* 2003;37(18):4060–9.
- [6] Haselden A, Christoforou C, Schlautman M. Characterization of airborne brake wear debris. *Final Rep* 2006:1–55.
- [7] Hulskotte JHJ, van der Gon HACD, Visschedijk AJH, Schaap M. Brake wear from vehicles as an important source of diffuse copper pollution. *Water Sci Technol* 2007;56(1):223–31.
- [8] Zhao H, Yin C, Chen M, Wang W. Risk assessment of heavy metals in street dust particles to a stream network. *Soil Sediment Contam An Int J* 2009;18(2):173–83.
- [9] Davis AP, Shokouhian M, Ni S. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 2001;44(5):997–1009.
- [10] Sandahl JF, Baldwin DH, Jenkins JJ, Scholz NL. A sensory system at the interface between urban stormwater runoff and salmon survival. *Environ Sci Technol* 2007;41(8):2998–3004.
- [11] Azizishirazi A, Dew WA, Forsyth HL, Pyle GG. Olfactory recovery of wild yellow perch from metal contaminated lakes. *Ecotoxicol Environ Saf* 2013;88:42–7.
- [12] Garg BD, Cadle SH, Mulawa PA, Groblicki PJ, Laroo C, Parr GA. Brake wear particulate matter emissions. *Environ Sci Technol* 2000;34(21):4463–9.
- [13] Hansen JA, Rose JD, Jenkins RA, Gerow KG, Bergman HL. Chinook salmon (*Oncorhynchus tshawytscha*) and rainbow trout (*Oncorhynchus mykiss*) exposed to copper: neurophysiological and histological effects on the olfactory system. *Environ Toxicol Chem* 2009;18(9):1979–91.
- [14] Hara TJ, Law YMC, Macdonald S. Effects of mercury and copper on the olfactory

- response in rainbow trout, *Salmo gairdneri*. *J Fish Res Board Canada* 1976;33(7):1568–73.
- [15] WHO WHO(. Particulate matter. 2000.
- [16] Ciudin R, Verma PC, Gialanella S, Straffelini G. Wear debris materials from brake systems: environmental and health issues. *WIT Trans Ecol Environ* 2014;191:1423–34.
- [17] Ghio AJ, Cohen MD. Disruption of iron homeostasis as a mechanism of biologic effect by ambient air pollution particles. *Inhal Toxicol* 2005;17(13):709–16.
- [18] Kukutschová J, Roubíček V, Malachová K, Pavličková Z, Holuša R, Kubačková J, et al. Wear mechanism in automotive brake materials, wear debris and its potential environmental impact. *Wear* 2009;267(5–8):807–17.
- [19] 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. *Environ Pollut* 2015;207:211–9.
- [20] Gilardi R, Alzati L, Thiam M, Brunel JF, Desplanques Y, Dufrénoy P, et al. Copper substitution and noise reduction in brake pads: graphite type selection. *Materials (Basel)* 2012;5(11):2258–69.
- [21] Aranganathan N, Bijwe J. Special grade of graphite in NAO friction materials for possible replacement of copper. *Wear* 2015;330:515–23.
- [22] Gu H, Chun KM, Song S. The effects of hydrogen on the efficiency of NOx reduction via hydrocarbon - selective catalytic reduction (HC - SCR) at low temperature using various reductants. *Int J Hydrogen Energy* 2015;40(30):9602–10.
- [23] Cho MH, Ju J, Kim SJ, Jang H. Tribological properties of solid lubricants (graphite, Sb₂S₃, MoS₂) for automotive brake friction materials. *Wear* 2006;260(7–8):855–60.
- [24] Martínez Maite A, Echeberria J, Loreto D, Antonio, Zanon, Matteo Rampin, Ilaria. Joint Development of copper-free low steel brake pads for light vehicles. Conference paper eurobrake. 2014. EB2014-DF-002: 1–9.
- [25] Jang H, Ko K, Kim SJ, Basch RH, Fash JW. The effect of metal fibers on the friction performance of automotive brake friction materials. *Wear* 2004;256(3–4):406–14.
- [26] Leonardi M, Menapace C, Matějka V, Gialanella S, Straffelini G. Pin-on-disc investigation on copper-free friction materials dry sliding against cast iron. *Tribol Int* 2018;119:73–81.
- [27] Mahale V, Bijwe J, Sinha S. A step towards replacing copper in brake-pads by using stainless steel swarf. *Wear* 2019;424–425:133–42.
- [28] Matějka V, Fu Z, Kukutschová J, Qi S, Jiang S, Zhang X, et al. Jute fibers and powdered hazelnut shells as natural fillers in non-asbestos organic non-metallic friction composites. *Mater Des* 2013;51:847–53.
- [29] Lee PW, Filip P. Friction and wear of Cu-free and Sb-free environmental friendly automotive brake materials. *Wear* 2013;302(1–2):1404–13.
- [30] Xin X, Xu CG, Qing LF. Friction properties of sisal fibre reinforced resin brake composites. *Wear* 2007;262(5–6):736–41.
- [31] Yun R, Filip P, Lu Y. Performance and evaluation of eco-friendly brake friction materials. *Tribol Int* 2010;43(11):2010–9.
- [32] Menapace C, Leonardi M, Matějka V, Gialanella S, Straffelini G. Dry sliding behavior and friction layer formation in copper-free barite containing friction materials. *Wear* 2018;398–399:191–200.
- [33] Aranganathan N, Mahale V, Bijwe J. Effects of aramid fiber concentration on the friction and wear characteristics of non-asbestos organic friction composites using standardized braking tests. *Wear* 2016;354–355:69–77.
- [34] Mahale V, Bijwe J, Sinha S. Influence of nano-potassium titanate particles on the performance of NAO brake-pads. *Wear* 2017;376–377:727–37.
- [35] Mahale V, Bijwe J, Sinha S. Studies on friction mechanism of NAO brake-pads containing potassium titanate powder as a theme ingredient. *SAE Int J Mater Manuf* 2018;11(1):43–56.
- [36] Kumar M, Bijwe J. Non-asbestos organic (NAO) friction composites: role of copper; its shape and amount. *Wear* 2011;270(3–4):269–80.
- [37] Aranganathan N, Bijwe J. Development of copper-free eco-friendly brake-friction material using novel ingredients. *Wear* 2016;352–353:79–91.
- [38] Luc Smeets KSD, Bart van de Worp. Reduced cost and improved performance of NAO/non-steel and Low-steel disc pads by using Promaxon®-D. Conference paper eurobrake 2012; Dresden, Germany: 1–2.
- [39] Mahale V, Bijwe J, Sinha S. Application and comparative study of new optimization method for performance ranking of friction materials. *Proc Inst Mech Eng Part J J Eng Tribol* 2018;232(2):143–54.