ANKARA YILDIRIM BEYAZIT UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATION OF THE EFFECT OF SEPIOLITE CLAY, SILICA AEROGEL FILLERS AND CNSL CONTENT ON THE PROPERTIES OF ORGANIC BRAKE PAD COMPOSITES

M.Sc. Thesis by

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M.Sc. THESIS EXAMINATION RESULT FORM

We have read the thesis **"INVESTIGATION OF THE EFFECT OF SEPIOLITE CLAY, SILICA AEROGEL FILLERS AND CNSL CONTENT ON THE PROPERTIES OF ORGANIC BRAKE PAD COMPOSITES"** completed by **BORA ORAL** under the supervision of **ASST. PROF. ŞERİFE AKKOYUN** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis forthe degree of Master of Science.

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INVESTIGATION OF THE EFFECT OF SEPIOLITE CLAY, SILICA AEROGEL FILLERS AND CNSL CONTENT ON THE PROPERTIES OF ORGANIC BRAKE PAD COMPOSITES

ABSTRACT

Friction materials have an important place in both highways and railways. Brake pads are mainly produced by a mixture of four main groups of materials: binders, reinforcements, friction modifiers and fillers. Selecting these materials in appropriate ratios and optimizing them according to the desired properties of the final product has a crucial effect on both the mechanical and tribological properties of brake pads. It is seen in the literature that many different types of materials are used to improve these properties. In this study, sepiolite clay and silica aerogel, which to our knowledge was never used for this purpose, were used as alternative fillers in organic brake pad composite materials. Composites with different amounts of these fillers were prepared and their density, porosity, friction and wear properties were characterized. The effect of the content of cashew nut shell liquid (CNSL) on the properties of the composites was also investigated. The results show that, the sepiolite clay used as filler clearly increases the hardness of the composites, while the silica aerogel filler has a decreasing effect on the hardness. While both fillers did not show a significant effect on the friction coefficient level, they have a positive effect on the wear properties as they relatively decrease the specific wear rate. An improved friction stability was also observed for some compositions. It is well known that synergistic effects between different fillers can be used in friction materials. Sepiolite clay and silica aerogel combined with an optimum CNSL content are good candidate for future researches and uses in organik brake pad composites.

Keywords: Organic Brake Pads, Sepiolite Clay, Silica Aerogel, CNSL.

SEPİOLİT KİLİ, SİLİKA AEROJEL KATKILARI VE CNSL ORANININ ORGANİK FREN BALATA KOMPOZİTLERİNİN ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİNİN İNCELENMESİ

ÖZ

Karayollarında ve demiryollarında sürtünme malzemelerinin önemli bir yeri vardır. Fren balataları temel olarak bağlayıcılar, takviye elemanları, sürtünme düzenleyiciler ve katkılar olmak üzere dört ana grup malzemenin karışımı ile elde edilirler. Bu malzemelerin uygun oranlarda seçilip son üründen istenen özelliklere göre optimize edilmesi fren balatalarının hem mekanik hem de tribolojik özellikleri üzerine etkisi büyüktür. Bu özelliklerin iyileştirilmesinde literatürde birçok farklı türden malzemenin kullanıldığı ve özellikler üzerinde etkilerinin olduğu görülmektedir. Bu çalışmada katkı malzemelerine alternatif olarak farklı oranlarda sepiyolit kili ve bu alanda araştırmalarımıza göre daha önce hiç kullanılmamış olan silika aerojeller içeren organik fren balatası kompozitlerinde alternatif katkılar olarak kullanılmıştır. Farklı oranlarda katkı içeren kompozitler malzemeler hazırlanarak yoğunluk, porozite, sürtünme ve aşınma özellikleri karakterize edilmiştir. İlaveten kaju kabuğu yağı oranının kompozitlerin özellikleri üzerindeki etkisi de incelenmiştir. Sonuçlara göre, kullanılan sepiyolit kili katkısı net olarak numunelerin sertliğini arttırken silika aerojel katkısı sertlik üzerinde düşürücü etki göstermiştir. Her iki katkı da sürtünme katsayısı seviyesi üzerinde belirgin bir etki göstermezken aşınma üzerinde olumlu etkileri olduğu ve özgül aşınma oranını düşürdüğü görülmüştür. Bazı katkı oranlarında sürtünme kararlılığının iyileştiği gözlemlenmiştir. Sürtünme malzemelerinin karışımında sinerjik etkilerin olabildiği bilinmektedir. Sepiolite kili ve silika aerojelin en uygun CNSL oranı ile birleştirilerek organik fren balatalarının özelliklerinin iyileştirilmesi konusuda etkin olabilecekleri öngörülmektedir.

Anahtar sözcükler: Organik Fren Balataları, Sepiyolit Kili, Silika Aerojel, CNSL.

CONTENTS

NOMENCLATURE

Abbreviations

ASTM	American Society for the Testing of Materials
AG	Silica aerogel
AG0	Composition without silica aerogel
AG1	Composition containing 0.46 wt. % of silica aerogel
AG2	Composition containing 0.93 wt. % of silica aerogel
AG3	Composition containing 1.39 wt. % of silica aerogel
AG4	Composition containing 1.86 wt. % of silica aerogel
CNSL	Cashew Nut Shell Liquid
C0	Composition without CNSL
C2	Composition containing 2 wt. % of CNSL
C4	Composition containing 4 wt. % of CNSL
C6	Composition containing 6 wt. % of CNSL
C8	Composition containing 8 wt. % of CNSL
SP	Sepiolite clay
SP0	Composition without sepiolite clay
SP5	Composition containing 5 wt. % of sepiolite clay
SP10	Composition containing 10 wt. % of sepiolite clay
SP15	Composition containing 15 wt. % of sepiolite clay
SP20	Composition containing 20 wt. % of sepiolite clay
SEM	Scanning Electron Microscopy
PAN	Polyacrylonitrile
XRD	X-Ray Diffraction
Avg.	Average
kV	Kilovolt
MPa	MegaPascal
MJ	MegaJoule

mg	Milligram
mm	Millimeter
nm	Nanometer
N	Newton
Rpm	Revolutions per minute
V	Velocity, m/s, volume, cm^3
s	Second
F	Tangential force, N
µm	Micrometer
µ	Coefficient of friction
ρ	Density, g/cm^3

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CHAPTER 1

INTRODUCTION

Friction materials are crutial for human safety in passenger transport. During the development of friction materials the safety factor must be considered. Most of the performance criteria of friction products are related to safety. Friction materials are complex composites and may contain more than 10 ingredients. These ingredients can be classified into four classes, namely fibrous reinforcement, binder, filler and friction modifiers. The fibrous reinforcement mainly increases strength, stiffness, thermal stability and frictional properties. Fillers are low cost minerals whose main function is to increase the volume of friction lining and thus to reduce the overall cost on a volume basis. Organic brake pads belongs to friction materials and are widely used in various applications. The improvement of their properties is a topic that still attracts many researchers. An efficient way to improve the properties of composites is the addition of fillers.

1.1 Literature Survey

1.1.1 Organic Brake Pads

1.1.1.1 Requirements of Friction Materials

The basic requirement of friction materials is that they should behave similarly during braking under all operating conditions. They should maintain their structural integrity and have a good durability. Moreover, the wear performance of both the friction material and the counter-surface is one of the main factors in brake pad development. The properties required from an ideal friction material are summarized below [1,2,3,4]:

- A minimum sensitivity to environmental conditions (Moisture, salt, mud, oil etc.)
- A minimum pad and counterface wear
- A low price
- A good resistance to fade
- A good recovery

- Braking without vibration and squeal noise
- Should not contain asbestos

1.1.2 Formulation of Brake Pads

There are many types of friction materials, depending on the application area. There are more than 10 components in a brake friction material. Each of these ingredients serves different purposes. The ingredients used in the production of friction materials are generally considered in 4 main categories [2,5].

1.1.2.1 Binders

Binders play an important role for friction materials, aiming to preserve the structural integrity of the brake pad under mechanical and thermal stress. They are affordable thermoset materials with good friction levels and thermal stability. Binders used in friction materials can be in liquid or powder form. Although novolac type phenolic resins are generally used, various modified resins can be used to increase the friction performance. Resins occupy around 20% by volume in formulations [6,7]. According to Yanar et al. an increases of the resin content into the system decreases the friction coefficient and the fade resistance of brake pad comosites [8].
Phenolics are the most commonly used resin binders in organic brake pads. They are obtained from the reaction between phenol and formaldehyde. A Novolac type resin is obtained if the reaction occurs in an acidic environment whereas a basic environment leads to a Resol type resin. The structures of those two resins and the schematic representation of the reactions involved are presented in Figure 1.1 When the phenolic resin is cured, a cross-linked thermosetting matrix that withstands relatively high temperatures is obtained.

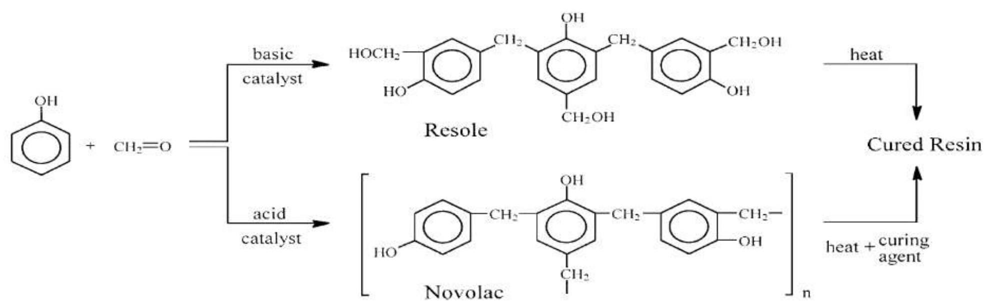

Figure 1. 1 Schematic representation of the reactions involved in the synthesis of Novolac and Resol resins [9].

1.1.2.2 Reinforcements

The purpose of reinforcement fibers is to provide mechanical strength to the friction material [2].

Asbestos, an inexpensive fiber reinforcement material with excellent thermal stability was used as a reinforcement element in friction materials for a long time, from the early 1900s until it was banned for its carcinogenic effects in 1980. After its ban, producers searched for alternative to asbestos [6]. The research showed that fibers have an effect on many parameters such as friction stability, fade resistance, wear and noise. It has been shown by Erikson et al. [10] that wear debris accumulates around the steel fibers and generates plateau areas and only these areas are in contact between the pad and the disc.

In addition, Yanar et al. observed that the fade resistance was improved and that the mechanical properties decreased with the increase in the ratio of steel fibers [11].

Other studies showed that organic fibers improved toughness and strength of brake pad composites. Therefore, organic fibers such as aramid fiber, carbon fiber, polyacrylonitrile (PAN), cellulose fiber were combined with mineral and ceramic fibers to become an alternative to asbestos [12].

Moreover, rock wool, which is a mineral wool is composed of inorganic fibers. It is obtained from molten rock at about 1600 °C by blowing air. It is known that the rock wool reduces heat transfer from the counterface during braking in brake pad applications owing to its insulating properties [13].

Another type of reinforcement used in organic brake pads are ceramic fibers that are usually produced from alumina or silicon carbide. These fibers have a very high thermal resistance. Due to their high strength to weight ratio, they can be preferred instead of steel fibers [6].

Öztürk et al. investigated different types of fibers such as rock wool, ceramic fiber, E-glass fiber and steel fiber. The authors showed that the highest friction coefficient and wear rate were obtained in compositions containing E-glass fibers and steel fibers. In addition, they observed that there is no direct relationship between mechanical properties and friction characteristics [14].

1.1.2.3 Friction Modifiers

Friction modifiers are used to give desired properties in friction materials. Lubricants and abrasives are used as friction modifiers. Lubricants are used to regulate the friction coefficient and control wear and temperature rise. Graphite is one of the most widely used lubricants. It can be natural or synthetic in powder or flake form. The excessive use of graphite has been shown to weaken the bond strength and shear strength of the phenolic resin [6,15]. Metal sulphides are also used as solid lubricants in brake pads. Cho et al. [16] investigated the effect of graphite and different types of metal sulphides on properties such as friction stability, wear and fade resistance. They showed that compositions containing antimony sulphide had better fade resistance than graphite containing ones and this was attributed to the formation of Sb_2O_3 at the sliding interface of the composites containing antimony sulfide.

Concerning the abrasives, these materials increase the friction coefficient but also the wear of the counter disc surface. They allow to remove the iron oxide film layer formed during friction and the Mohs hardness is around 7-8. Abrasives such as zircon, quartz, alumina, magnesia, zirconia, zeolite, silicon carbide are used in commercial brake pads. Their use in high amounts causes sudden fluctuations in the friction coefficient, therefore the composite exhibits an unstable braking performance [6,17].

Another friction modifier used in organic brake pad composites is the Cashew Nut Shell Liquid (CNSL). It is obtained from the cashew shell and contains various phenolic components. CNSL is a dark viscous oil and has a characteristic odor. It is insoluble in water but soluble in many organic solvents. It generally consists of 4 main components: Cardanol, cardol, anacardic acid and 2-methyl cardol [18].

The phenolic properties of CNSL are used to make the condensation polymer. Both novolac and resol resins can be produced from it. CNSL has long side chain groups providing ita flexible structure. This long aliphatic side chain also provides hydrophobic properties. It improves fade resistance, which is a desired property in brake pad formulations. It is compatible with many polymers such as melamine, polyester alkyds. Moreover, CNSL mixes well with rubber and other natural or synthetic polymers. CNSL also has excellent properties for brake pad applications with its properties such as absorption of heat generated by friction, longer braking efficiency, and high impact resistance [19].

1.1.2.4 Fillers

Fillers are chosed depending on the type of the friction material. For example, very high brake noise occurs in braking with high metal ratio, and fillers such as mica, vermiculite, rubber are preferred for the absorption of this noise. Barium sulphate, the most widely used filling material, provides thermal stability to the brake pads. As an alternative to barium sulphate, calcium carbonate similarly provides thermal stability and improves fade resistance. Mica is another widely used filling material. It is added to compositions to suppress low frequency brake noises. Vermiculite is also used as a noise blocker and to control the density. Organic fillers such as friction dust and rubber reduce brake noise by increasing the contact surface of the brake pad owing to their viscoelastic properties [6].

1.1.3 Tribology

The term ‘Tribology’ derives from the Greek word ‘tribos’ which means rubbing. Tribology would be literally translated as the science of rubbing. It can be defined as ‘The science and technology of interacting surfaces in relative motion and related subjects and particles.’ Tribology is a field of science that requires multidisciplinary knowledge such as physics, chemistry, materials science, thermodynamics, rheology, applied mathematics to understand interface interactions. It is critical for sliding and rolling machine parts including brakes, clutches, bolts as well as nuts.

The aim of tribological research is to minimize the inefficiencies caused by friction and wear, to be more economical with more performance and less breakdown [20].

1.1.3.1 Friction

The friction force can be defined as the resistance an object encounters while moving on another. These movements are divided into 2 important groups as sliding and rolling. In both cases, a tangential force F is required to move the solid body, as shown in Equation (1.1), and the ratio between this force and normal load W gives the coefficient of friction which is denoted by μ.

$$\mu . F = W \tag{1.1}$$

Most materials have a coefficient of friction in the range of 0.1 to 1 in an air and non-lubricating environment.
Friction is not a material property. Different results can be obtained depending on the conditions of the system, such as the contamination of the friction interfaces, the amount of liquid at the interfaces, the thin surface film, and the effect of lubricants [20].

1.1.3.2 Wear

Wear is the surface damage or material loss of one or both solid surfaces during movements such as sliding, rolling or impact. Mostly wear occurs through surface interaction in roughness. The definition of wear is based on material loss. Micro-sized material displacement in the body without a change in the weight and volume of the material is also considered as wear.
Wear as friction is not a material property. Operating conditions affect interface wear. High friction is assumed to cause high interface wear, but this is not necessarily true. For example, solid lubricants and polymers show low friction but relatively high wear. On the other hand, ceramics have very low wear with moderate friction [20].

1.1.4 Silica Aerogel

Aerogels that are nano porous soft materials, were discovered more than 90 years ago [21]. They are foam-like translucent materials. Aerogels are a unique material with a very large surface area with 99.9% of air. Silica aerogel is a widely used one and it posseses unique properties such as high specific surface area, high porosity, low density high thermal insulation value, ultra low dielectric constant and low index of refraction [22]. Some of its characteristics are gathered in Table 1.1.

Table 1. 1 Properties of silica aerogel [22].

Property	Value	Comment
Apparent density	0.003–0.35 g/cm^3	Most common density is ～0.1 g/cm^3
Internal surface area	600–1000 m^2/g	
% Solids	0.13–15%	Typically 5% (95% free space)
Mean pore diameter	～20 nm	As determined by BET method
Primary particle diameter	2–5 nm	Determined by electron microscopy
Refractive index	1.0–1.08	
Coefficient of thermal expansion	2.0–4.0 x 10−6	Determined using ultrasonic methods
Dielectric constant	～1.1	For a density of 0.1 g/cm^3
Sound velocity	100 m/s	For a density of 0.07 g/cm^3

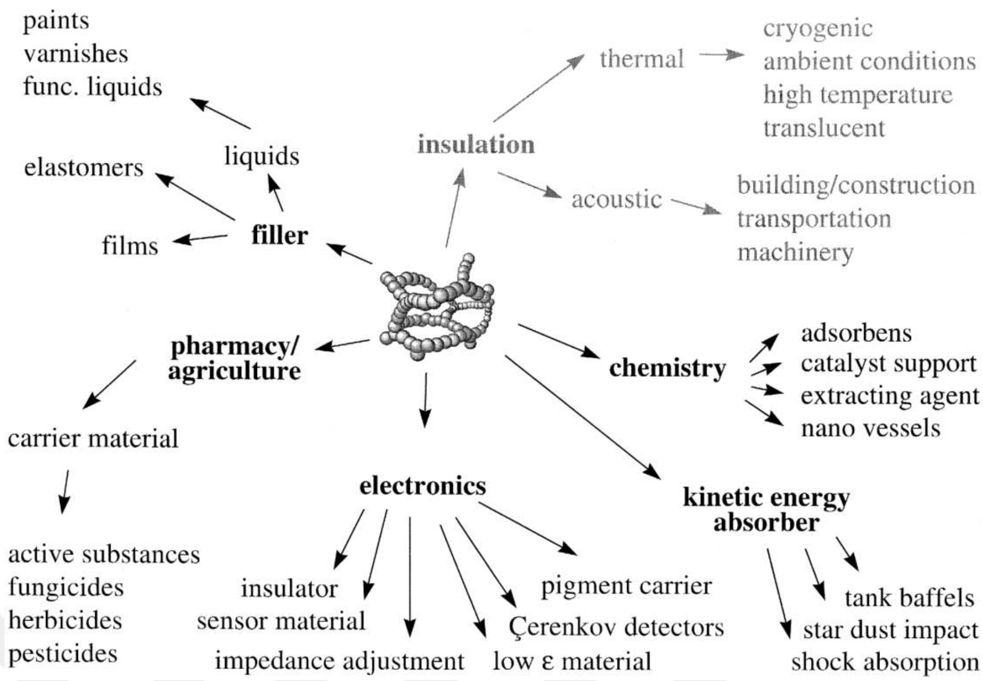

Figure 1. 2 Application fields for silica aerogel [21].

1.1.5 Sepiolite Clay

Sepiolite is a natural clay mineral with a fibrous structure composed of magnesium hydrosilicates in the sepiolite-palygorskite group. Sepiolite is also called as attapulgite [23]. Two types exist in nature. The first one is the hydrothermal type α-sepiolite and the second one is the sedimentary type β-sepiolite. β-sepiolite has a fibrous structure similar to asbestos [24,25]. Because of these properties, its use as an alternative to asbestos in brake composite was investigated by Kai hou et al [25] and other researchers.

1.1.6 Use of Cashew Nut Shell Liquid, Sepiolite Clay and Silica Aerogel in Organic Brake Pads

Although studies on the use of cashew dust or friction dust, which are the powder form of CNSL, are present in the literature, studies on the use of CNSL in liquid form are quite few. Besides, it has been shown that CNSL increases the wear resistance in brake linings. It decreases the elastic modulus and is a renewable source [30,31].

According to the literature, the use of sepiolite in lining applications can be an alternative to asbestos as a reinforcement material due to its fibrous structure. It has been shown that surface modified sepiolite fibers improve the mechanical properties and reduce the wear rate [25]. In addition, certain rates of sepiolite have been shown to reduce the wear rate in bronze-based brake linings [33].

To our knowledge, the effect of silica aerogel on brake linings has not been studied yet. Nevertheless, friction tests on polypropylene / silica aerogel composites showed that the amount of wear decreased, the thermal stability increased and the mechanical properties were weakened in composite filled with silica aerogel [32].

1.2 Aim of the Thesis

In this study, the effect of sepiolite clay, silica aerogel and CNSL content on the different properties of organic brake pad composites were investigated. The aim was to improve the friction and wear properties of the linings with these fillers and to optimize the compositions.

1.3 Original Contribution

This study proposes a new appraoch associating the use of different sepiolite clay filler contents and various liquid CNSL contents in organic brake pad composites. To our knowledge the effects of these combinations on the properties of organic brake pads were not investigated before. Especially, no study exist on the use of amounts of CNSL as high as 6 wt. % or 8 wt. %. Another originality of this work resides in the use of silica aerogel as filler in organic brake pad composites.

CHAPTER 2

MATERIALS AND METHODS

In this study, 14 different raw materials of various particle sizes, morphology, density and hardness were used in the basic formulation. In accordance with the confidentiality agreement made with the Metisafe, the formulations used in the study will not be presented in detail.

2.1 Materials

As mentioned in Chapter 1, the composites prepared in this study are composed of materials that can be classified into four groups.

2.1.1 Binder

2.1.1.1 Phenolic resin

Phenolic resins are the most commonly used binder in brake pads. A Novolac type phenolic resin and its Hexamine curing agent were supplied from Çukurova Kimya. The properties of the phenolic resin provided by the supplier are gathered in Table 2.1.

Table 2. 1 Properties of phenolic resin.

Hexamine content (wt. %) ISO 8988	**Flow distance 125 °C (mm) ISO 8619**	**Softening point (°C) ISO 3146**	**Sieve (-45) Micron (%)**
8.3-8.9	29-33	94-96	95-99

2.1.2 Reinforcements

2.1.2.1 Glass Fiber

Glass fibers supplied from Şişecam (Turkey) were used as reinforcement. The characteristics of glass fiber are presented in Table 2.2.

Table 2. 2 Properties of glass fiber.

Material properties	**Value**
Glass type	E
Fiber diameter (µm)	Avg. 13
Fiber length (mm)	3-4.5
Moisture content (%)	Max 0.07

2.1.2.2 Rockwool

Rock wool supplied from Lapinus was used in this study. The characteristics of rock wool are presented in Table 2.3.

Table 2. 3 Properties of rock wool.

Material properties	**Value**
Non-fibrous Material (%wt)	Max 5.0
Fiber length (µm)	125 ± 50
Moisture content (%)	Max 0.1

2.1.3 Friction Modifiers

2.1.3.1 Graphite

The main purpose of its use in brake pads is to stabilize the friction coefficient. It facilitates the dissipation ofthe heat generated during braking. Natural graphite was used in this study and was supplied from Skaland graphite.

2.1.3.2 Cashew Nut Shell Liquid

The cashew nut shell liquid (CNSL) was purchased from Çukurova Kimya. The characteristics of CNSL are presented in Table 2.4. A picture of CNSL is given in Figure 2.1.

Table 2. 4 Properties of CNSL.

Density (g/cm^3)	**B time 150 °C %10 hexamine (min)**	**Viscosity (mPa.s)**	**pH**
0.94-0.98	9-18	200-600	6

Figure 2. 1 Picture of the Cashew Nut Shell Liquid.

2.1.3.3 Friction Dust

Friction dust is the cured powder form of CNSL. It provides stability in the friction coefficient and also reduces brake noise. The friction dust used in this study was supplied from Zem Kimya (Turkey).

2.1.4 Fillers

2.1.4.1 Steel Powder

Steel powder is used as a filler in friction materials, it helps to dissipate heat and affects the performance by increasing thermal conductivity. Steel powder was supplied from BÜNSA (Turkey). The particle size is 300 µm.

2.1.4.2 Brass

It has been observed that the use of soft metal particles such as brass in brake pads increases the thermal conductivity, stabilizes the coefficient of friction and reduces pad wear. Brass supplied from a local supplier. The average particle size provided by the supplier is 600 µm.

2.1.4.3 Barium Sulphate

Also known as barite barium sulfate is a space filler material used for the thermal stability of the composites. Barium sulphate (5 micron fine powder) was supplied from Işık madencilik (Turkey).

2.1.4.4 Sepiolite Clay

Sepiolite clay (SP) is a hydrated magnesium silicate mineral. It is a white powder (Figure 2.2) which has a micro porous and fibous structure as shown by the SEM micrograph in Figure 2.3. It provides thermal stability under high temperature conditions. Sepiolite clay was supplied from Dolsan madencilik (Turkey). Average fiber lenght is 100 nm and average fiber diameter is 5 nm. A picture of SP is given in Figure 2.2. The XRD pattern of SP is also presented in Figure 2.4.

Figure 2. 2 Picture of sepiolite clay powder.

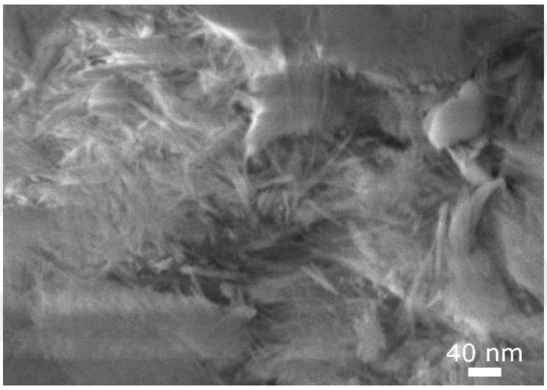

Figure 2. 3 SEM micrograph of sepiolite clay.

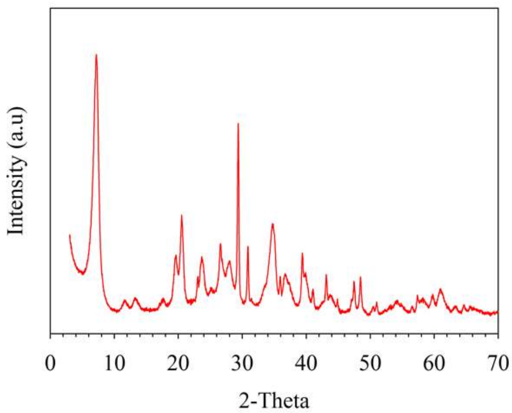

Figure 2. 4 XRD pattern of sepiolite clay.

2.1.4.5 Silica Aerogel

Silica aerogel (AG) (Levron) was kindly provided by Megateknik. According to the supplier, the AG particles have a surface area between 700-800 m^2/g and they present a heat conductivity factor of 0.016 W/m.K. In this study, AG was used into a powder form as illustrated in Figure 2.5. The SEM micrograph of AG agglomerates is given in Figure 2.6. The XRD pattern presented in Figure 2.7 shows an amorphous structure.

Figure 2. 5 Picture of silica aerogel.

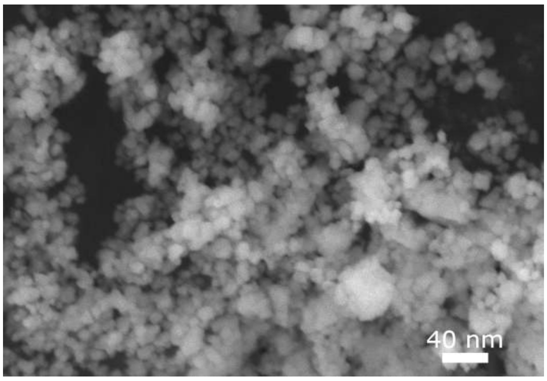

Figure 2. 6 SEM micrograph of silica aerogel.

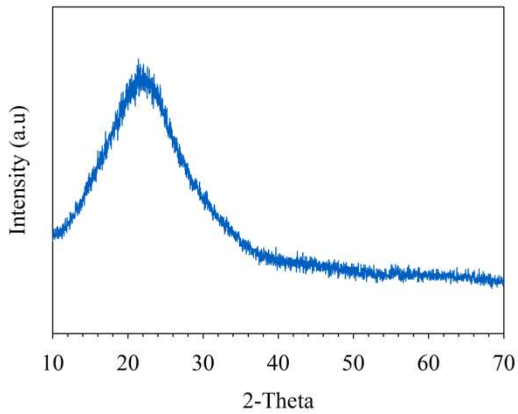

Figure 2. 7 XRD pattern of silica aerogel.

2.2 Formulations and Processing of Composite Samples

In the first part of the study, in order to determine the optimum content of CNSL, composite samples containing various amounts of CNSL and two different contents of SP and AG fillers were prepared. For this purpose, samples where 2 wt. %, 4 wt. %, 6 wt. % and 8 wt. % of CNSL was added to the basic formulation (presented in Table 2.5) were made. Then, various contents of sepiolite clay or silica aerogel were added to each the mixtures.

In the case of SP containing composite samples, formulations with a sepiolite clay content of 5 wt. % and 20 wt. % (denominated as SP5 and SP20, respectively) were realized. Sepiolite and silica aerogel ratios used were adjusted to be equal volumetrically to each other. Therefore, the corresponding amounts of aerogel were: 0.46 g of silica aerogel for 5 wt. % of SP, and 1.86 g of silica aerogel for 20 wt. % of SP.

After the determination of the optimal CNSL content, in a second part of the study, the effect of SP content with the optimal CNSL content was investigated. For this purpose, composites with a fixed content of CNSL (optimal content) and various contents of SP (5 wt. %, 10 wt. %, 15 wt. % and 20 wt. %) were prepared. All the formulations are summarized in Table 2.6.

Then, in a next part, the effect of AG content with the optimal CNSL content was examined and composites with a fixed content of CNSL (optimal content) and various contents of AG were prepared. Similarly to the first part of the study, SP and AG ratios used were adjusted to be equal volumetrically to each other. The correspondences are as follows: 0.46 g of silica aerogel (AG1) for 5 wt. % of SP, 0.93 g of silica aerogel (AG2) for 10 wt. % of SP, 1.39 g of silica aerogel (AG3) for 15wt. % of SP and 1.86 g of silica aerogel (AG4) for 20 wt. % of SP. All the formulations are summarized in Table 2.7.

The processing of the organic brake pad omposites was performed as follows:
The fiber reinforcement components and CNSL were mixed by hand. Then, the fibers were opened up with a mixer for 1 minute. A conventional high-speed twin blade mixer was used at 1200 rpm. The other components were added and the whole was mixed for 5 minutes to obtain homogeneous mixtures.
Afterwards the particular amount of mixture was pressed under the pressure of 50 bar. The temperature of preheated mold was 90 °C and was increased to 160 °C and the samples were cured in the mold under a pressure of 50 bar for 10 min. Finally, the samples were post-cured at 180 °C for 1 hour to completely cure all of the resin into the sample. The sample sizes of the pins prepared for friction tests was 20 mm in diameter and 15 mm in thickness.

Table 2. 5 Base formulation.

Material	**Weight (%)**
Binders	10
Reinforcements	8.5
Friction Modifiers	21.5
Fillers	60

Figure 2. 8 Picture of raw materials.

Table 2. 6 Formulations of composites containing sepiolite clay (SP).

Sample No	Binder	Reinforcements	Friction Modifiers	Fillers	CNSL	Sepiolite
C0SP0AG0	10	8.5	21.5	60	0	0
C0SP5AG0	10	8.5	21.5	55	0	5
C0SP10AG0	10	8.5	21.5	50	0	10
C0SP15AG0	10	8.5	21.5	45	0	15
C0SP20AG0	10	8.5	21.5	40	0	20
C2SP0AG0	10	8.5	19.5	60	2	0
C2SP5AG0	10	8.5	19.5	55	2	5
C2SP20AG0	10	8.5	19.5	40	2	20
C4SP0AG0	10	8.5	17.5	60	4	0
C4SP5AG0	10	8.5	17.5	55	4	5
C4SP10AG0	10	8.5	17.5	50	4	10
C4SP15AG0	10	8.5	17.5	45	4	15
C4SP20AG0	10	8.5	17.5	40	4	20
C6SP0AG0	10	8.5	15.5	60	6	0
C6SP5AG0	10	8.5	15.5	55	6	5
C6SP20AG0	10	8.5	15.5	40	6	20
C8SP0AG0	10	8.5	13.5	60	8	0
C8SP5AG0	10	8.5	13.5	55	8	5
C8SP20AG0	10	8.5	13.5	40	8	20

Table 2. 7 Formulations of composites containing silica aerogel (AG).

Sample No	Binder	Reinforcements	Friction Modifiers	Fillers	CNSL	Silica Aerogel
C0SP0AG0	10	8.5	21.5	60	0	0
C0SP0AG1	10	8.5	21.5	59.54	0	0.46
C0SP0AG2	10	8.5	21.5	59.07	0	0.93
C0SP0AG3	10	8.5	21.5	58.61	0	1.39
C0SP0AG4	10	8.5	21.5	58.14	0	1.86
C2SP0AG0	10	8.5	19.5	60	2	0
C2SP0AG1	10	8.5	19.5	59.54	2	0.46
C2SP0AG4	10	8.5	19.5	58.14	2	1.86
C4SP0AG0	10	8.5	17.5	60	4	0
C4SP0AG1	10	8.5	17.5	59.54	4	0.46
C4SP0AG2	10	8.5	17.5	59.07	4	0.93
C4SP0AG3	10	8.5	17.5	58.61	4	1.39
C4SP0AG4	10	8.5	17.5	58.14	4	1.86
C6SP0AG0	10	8.5	15.5	60	6	0
C6SP0AG1	10	8.5	15.5	59.54	6	0.46
C6SP0AG4	10	8.5	15.5	58.14	6	1.86
C8SP0AG0	10	8.5	13.5	60	8	0
C8SP0AG1	10	8.5	13.5	59.54	8	0.46
C8SP0AG4	10	8.5	13.5	58.14	8	1.86

2.3 Characterization

2.3.1 Hardness

The first attempts to characterize the hardness of the composite samples were made using a Shimadzu HMV-G Micro Vickers hardness tester. However, they were unsuccessful. Therefore, the shore D hardness of each sample was determined using a Shore durometer. The measurements were realized at room temperature and three replicates were used for each case.

2.3.2 Density and Porosity

The density (ρ) of the samples was determined through the mass and volume of the samples according to formula:

$$\rho = \frac{m}{V}, \quad \textbf{(2.1)}$$

Where *m* and *V* are the mass and the volume of the samples respectively.
Then, the porosity of the composites was calculated using the Archimedes'principle, according to the procedure in ASTM C373-88 standard and using equation 2.2.

$$\%P = \frac{M\text{-}D}{M\text{-}S} \times 100 \quad \textbf{(2.2)}$$

Where P is the apparent porosity, D is the dry mass, M is the saturated mass and S is the mass suspended in water. After heating, the dry mass (D) of samples was measured with a precision balance with an accuracy of 0.001 g. The samples were stored in distilled water for 3 days. After impregnation, the saturated mass (M) and the mass suspended mass in water (S) were measured using the same balance. For each case, three replicates were used.

2.3.3 X-Ray Diffraction (XRD)

X-ray diffraction patterns of the sample were recorded using a Rigaku miniflex-600 X-ray diffractometer using a Kα radiation of Cu, (λ=1.54Å) at a scan rate of 0.02°/s.

2.3.4 Scanning Electron Microscopy (SEM)

The morphology of the worn surface of brake pad composites was investigated by scanning electron microscopy (SEM) with a Hitachi FlexSEM 1000 II microscope at voltages of 5, 10 and 15 kV.

2.3.5 Friction and Wear Test

An in-house pin-on-disc type test system was used to perform friction and wear tests on the brake pad composite. The measurements were realized on three replicates for each sample. For this purpose, a rotating disc at a speed of 2118 rpm, corresponding to a sliding speed of 20 $m.s^{-1}$ was used. During braking, periods where a pressure of 0.6 MPa was applied to the samples by means of a hydraulic cylinder for 20 s and then removed for 90 s were repeated fifteen times. The coefficient of friction (μ) was recorded during the tests as a function of time and applied loads. The wear loss was measured using a precision balance with an accuracy of 0.001 g.
The specific wear rate of samples calculated as follow:

$$W_v = \frac{(w_i - w_f) \times 10^6}{\rho \times F_N \times \mu_{avg} \times V \times t} \tag{2.3}$$

Where, W_v is the specific wear rate in cm^3/MJ, μ_{avg} is the average friction coefficient, w_i is the initial weight in g, V is the velocity in m/s, w_f is the final weight in g, t is the time in s, ρ is the density of the sample in g/cm^3 and F_N is the applied load in N.

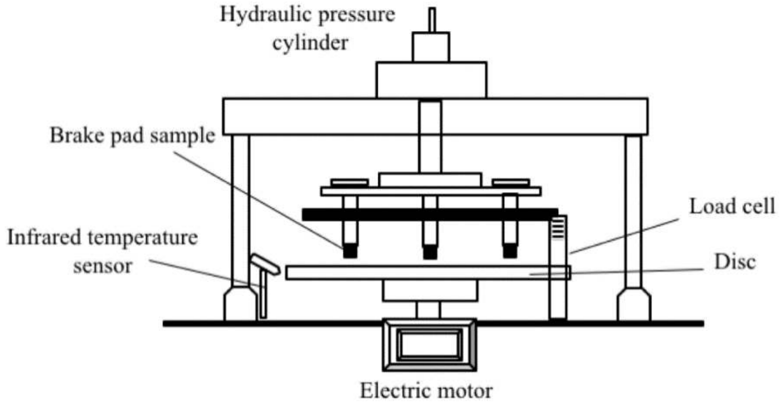

Figure 2. 9 Schematic representation of a pin on disc system [26].

Figure 2. 10 Picture of the pin on disc apparatus.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Effect of CNSL Content on the Properties of Brake Pad Composites

In this section, the effect of various CNSL content (0, 2, 4, 6 and 8 wt. %) on the properties of the composites was investigated. The aim is to determine the optimal CNSL content. For all the samples considered in this section, the amounts of SP or AG fillers are fixed. Only the CNSL content varies for each composition. For simplicity and clearness, in the case of both fillers, results obtained for samples with no filler (SP0 and AG0), samples with a low content of filler (SP5 and AG1) and samples with a high content of filler (SP20 and AG4) are presented.

3.1.1 Effect on the Density

Figure 3.1 shows the effect of CNSL content on the density of the composites for samples without sepiolite clay (SP0), with a low content of sepiolite clay (SP5) and with a high content of sepiolite clay (SP20). In all cases, an increase of the density is observed with increasing CNSL content. The highest density of 2.27 g/cm^3 was observed with the sample containing 5 wt. % SP and 8 wt. % of CNSL. For samples without SP and those containing 5 wt. % of SP, the density remains almost constant and around 2.2 g/cm^3 until 4 wt. % of CNSL. Then, a slight increase is observed for higher CNSL contents. However, this trend is not valid for samples containing 20 wt. % of SP which present a noticeable increase from 1.98 g/cm^3 to 2.24 g/cm^3 until 6 wt. % of CNSL content and decreases. It should be noticed that among composites with no CNSL content the sample with 20 wt. % of SP has a very low density (1.98 g/cm^3) compared to the cases without SP and with 5 wt. % of SP. Then, the gap between SP20 samples and the other two groups is almost filled at 6 wt. % of CNSL but it rises again for higher CNSL content. These evolutions clearly show that CNSL stabilizes the density of the system. As this resin is liquid, it probably wets the fillers and improve the interactions between the Novolac resin and different components of the mixture.

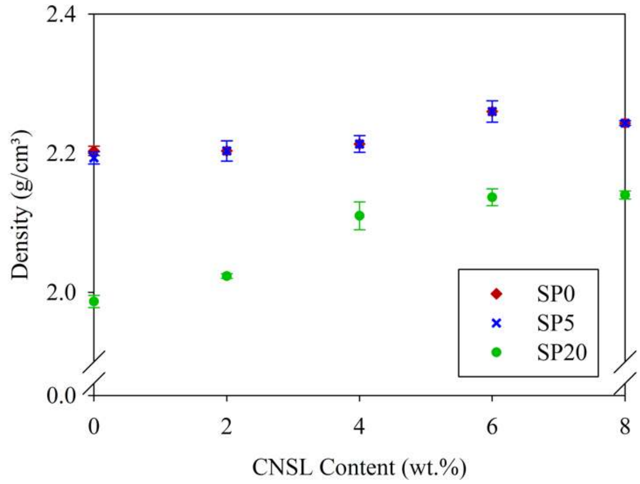

Figure 3. 1 Density of sepiolite clay containing samples with various CNSL ratios.

As presented in Figure 3.2, although a slight increase of the density is observed with increasing CNSL content, the effect of CNSL content on the density of samples containing silica aerogel is not as pronounced as in the case of SP containing samples. It can also be noticed that the three different graphs converge to a same density of 2.25 g/cm^3 with a CNSL content of 8 wt. %. The highest density was obtained at 2.25 g/cm^3 with 8% CNSL and the lowest density with 2.13 g/cm^3 in the formulations without CNSL. Moreover, the density of samples containing silica aerogels (AG1 and AG4 with various CNSL content) is lower compared to samples without AG (AG0 samples with different CNSL amounts). This evolution is in correlation with the literature [27] and is probably due to the high porosity of AG filler and its low bulk density which induces a lower density for samples containing AG. The effect of CNSL ratio on density can be related to the amount of wetness of the raw mixture. The wetter mixtures gained more compressibility, thus containing more substance per unit volume, resulting in an increase in density in the material.

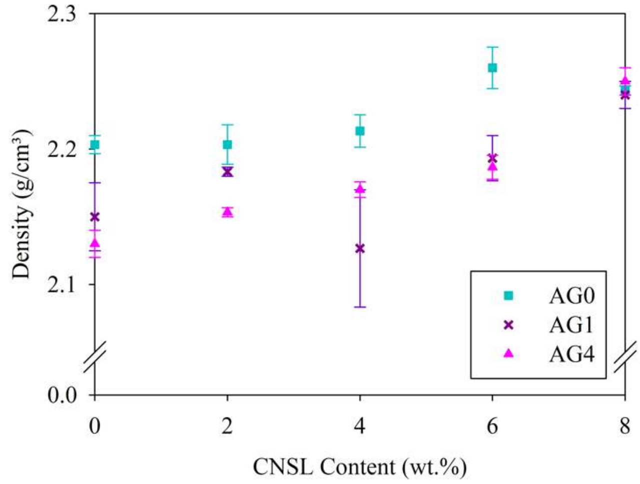

Figure 3. 2 Density of silica aerogel containing samples with various CNSL ratios.

3.1.2 Effect on the Porosity

The effect of CNSL content on the porosity of SP containing composites is presented in Figure 3.3. According to this figure, the porosity decreased as the CNSL ratio increased. Samples with no SP and 5 wt. % of SP exhibit a relatively similar pattern as they both slightly decrease. However, the effect of 20 wt. % of sepiolite clay on the porosity is obvious as a decrease from 14% to 1.4% is observed with increasing CNSL content.

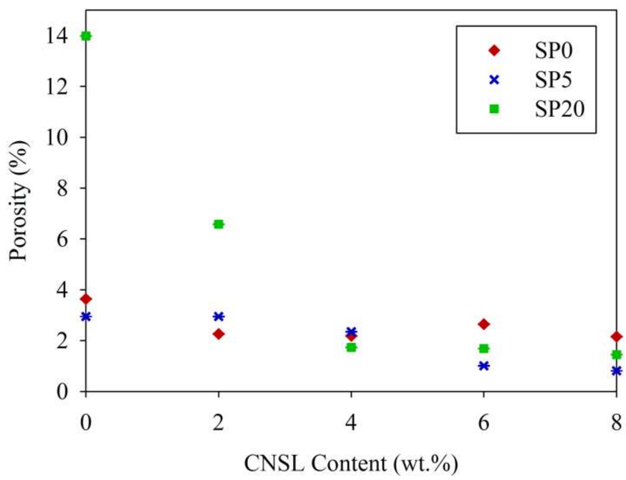

Figure 3. 3 Porosity of sepiolite clay containing samples with various CNSL ratios.

When the effect of CNSL content on the porosity of samples containing silica aerogel is examined (Figure 3.4), the general trend is that the porosity decreases with the increase of CNSL content. The composition containing 0.46 wt. % (AG1) silica aerogel presents a peak at 4 wt. % of CNSL, but with the increase in the CNSL ratio, a decrease in porosity is observed again. The porosity remains constant around 3% until 4% of CNSL ratio for samples with 1.86 wt. % (AG4) of silica aerogel. Then a significant decrease to 1.61% is observed with higher CNSL contents.

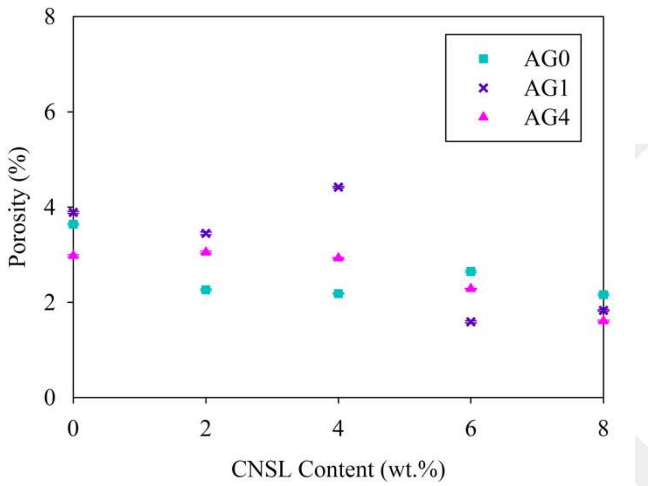

Figure 3. 4 Porosity of silica aerogel containing samples with various CNSL ratios.

In both cases, the effect of CNSL content on the porosity seems parallel to its effect on the density. Actually, the low value of the density of the SP20 sample without CNSL (see Figure 3.1) is probably due to the fact that the high amount of fibrous SP fillers induces the introduction of more voids into the system. When it is added into the formulation, the CNSL resin wets the fillers and improves the interfacial interactions between the different components of the composite. It can be assumed that the increase of CNSL content induces a less voided structure and therefore, the porosity decreases.

3.1.3 Effect on Shore D Hardness

The effect of CNSL content on shore D hardness of SP containing composites is presented in Figure 3.5. It can be seen that the sepiolite clay does not have a significant effect in the case of samples without CNSL as they have similar hardness values. No trend emerges for SP5 samples (with 5 wt. % of SP) because although the Shore D hardness is higher to the values obtained for SP0 samples (without SP) with increasing CNSL content, this evolution is inversed in the case of the SP5 sample containing 6 wt. % of CNSL. However, in the case of composites with a sepiolite clay amount of 20 wt. %, the increase in the CNSL content induces a rise of the Shore D hardness after 2 wt. % of CNSL and then it stabilizes and remains constant at 90 Shore D hardness. This behavior is in correlation with the literature. Farshchi and Ostad (2020) [28] showed that the increase of sepiolite content induced an increase of the hardness of recycled high density polyethylene / sepiolite clay composites.

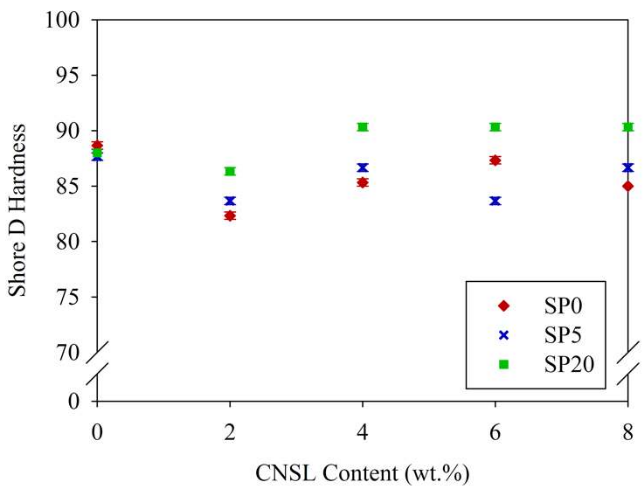

Figure 3. 5 Shore D hardness of sepiolite clay containing samples with various CNSL ratios.

Concerning the composites containing silica aerogel, as shown in Figure 3.6, the sample that does not contain neither CNSL nor AG (AG0 at CNSL content of 0%) has the highest Shore D hardness value. Moreover, in all compositions, the increase of CNSL content induces first a decrease of the hardness followed by an increase. It should be noticed that for samples AG0 and AG1, the hardness decreases until a CNSL content of 2 wt. % and then increases. However, in the case of the sample with the highest AG content (AG4), the onset of the increase is ‘delayed’ to a higher CNSL content of 4 wt. %. Besides, for CNSL contents higher than 2 wt. %, the samples filled with AG have a lower hardness compared to samples without AG (AG0 samples) until 8 wt. % of CNSL where all samples present approximately the same hardness.

It is well known that silica aerogel [27] and CNSL are hydrophobic [19,29]. Maghsoudi and Motahari investigated the properties of epoxy/silica aerogel composites. They showed that the increase of silica aerogel content induced an increased of the Shore D hardness of the composites [27]. However, in our study, the Shore D hardness of samples containing silica aerogel (AG1 and AG4) with different CNSL contents, is lower compared to samples without AG (AG0) with various amounts of CNSL. Actually, the composites prepared in our study are composed of many hydrophilic and hydrophobic components. The presence of CNSL increases the hydrophobicity of the system and therefore, improves the interactions between AG filler and the resin. Moreover, for AG0 samples (without AG) and AG1 samples (with 0.46 wt. % of AG) and increasing amount of CNSL, the hydrophobicity is prevalent in the whole system until 2 wt. % of CNSL. However, as mentioned by [27], for CNSL contents above a critical value, 2 wt. % in our case, the hydrophobicity becomes prevalent and therefore, interactions with hydrophobic AG particles are improved which induces an increase of the Shore D hardness. The shift of the critical CNSL content in the for AG4 samples containing 1.86 wt. % of AG can be attributed to the fact that as more hydrophobic AG particles are present, more CNSL is required to reach the hydrophilic – hydrophobic balance of the system.

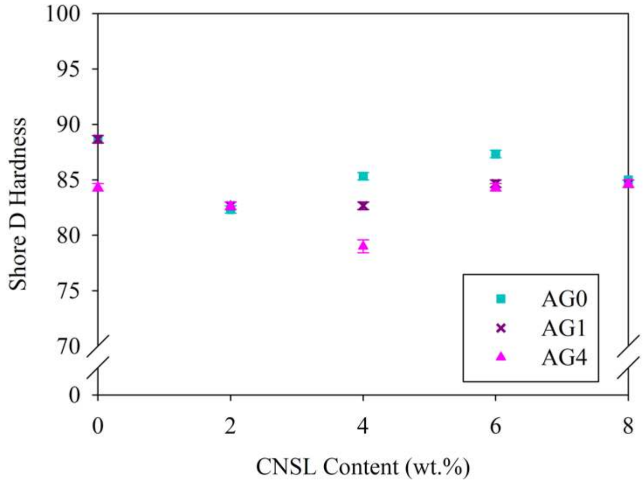

Figure 3. 6 Shore D hardness of silica aerogel containing samples with various CNSL ratios.

3.1.4 Evolution of the Friction Coefficient with Sliding Time

According to Figure 3.7, the increase of CNSL content does not seem to have an obvious effect on the friction characteristics and the friction coefficient stability in compositions without sepiolite clay filler.

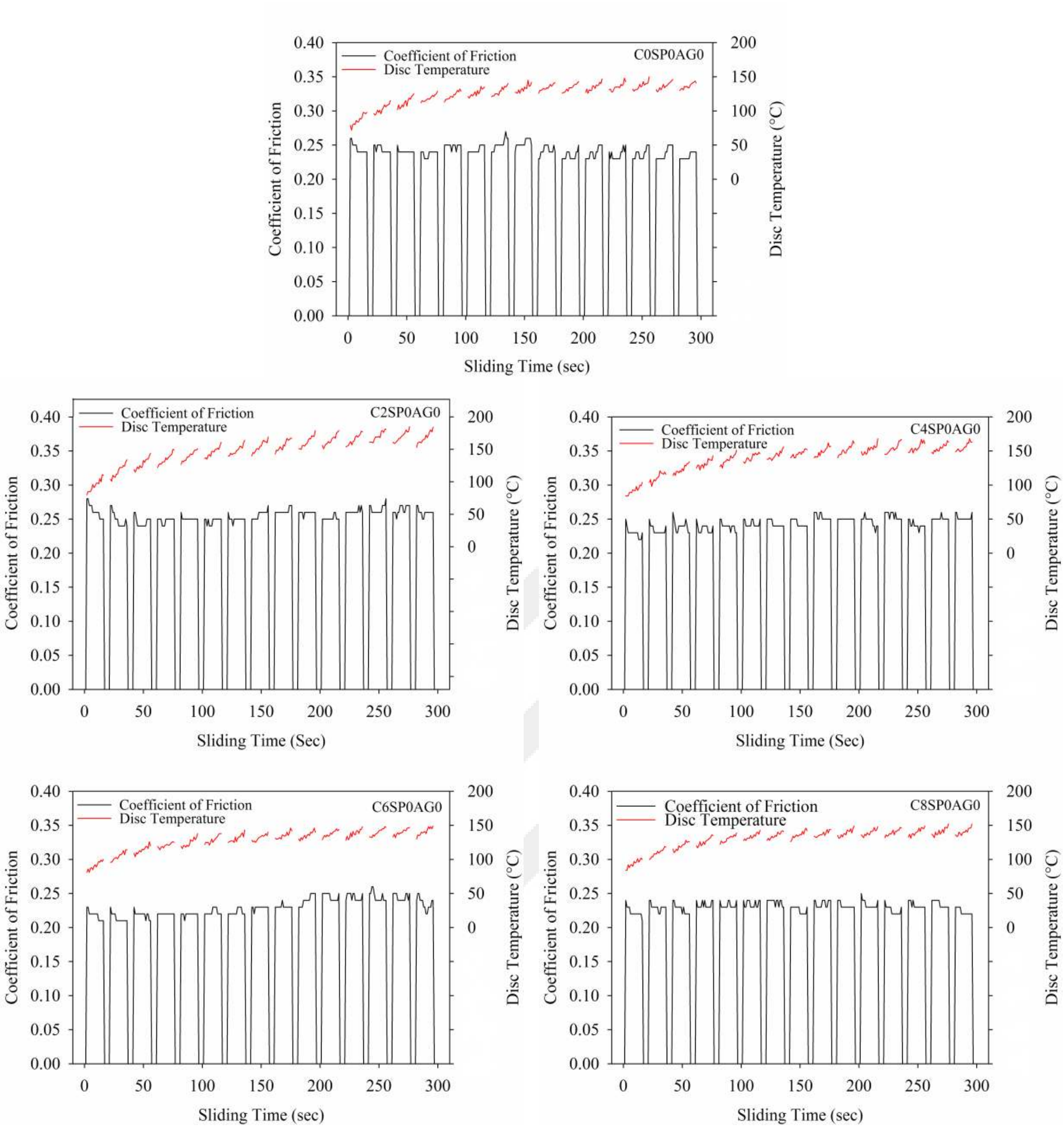

Figure 3. 7 Evolution of the coefficient of friction of samples without SP or AG and with various CNSL ratios.

Concerning samples containing 5 wt. % of SP, the evolution of the friction coefficient remains approximately constant until a CNSL content of 4 wt. %. Then, it evolves at higher values for the sample with 5 wt. % of SP and 6 wt. % of CNSL and finally, it seems stabilized at lower values. It should be noticed that for the sample containing no CNSL but 5 wt. % of SP, the disc temperature is at its higher level.

However, interestingly, in the case of the sample containing 6 wt. % of CNSL and 5 wt. % of SP, although the friction coefficient evolves at slightly higher levels as the previous sample, the disc temperature evolves at lower levels. Therefore, these results show that the CNSL improve the heat dissipation. Besides, for the sample containing 8 wt. % of CNSL and 5 wt. % of SP, the friction coefficient evolves at a lower level and the same tendency is observed for the disc temperature.

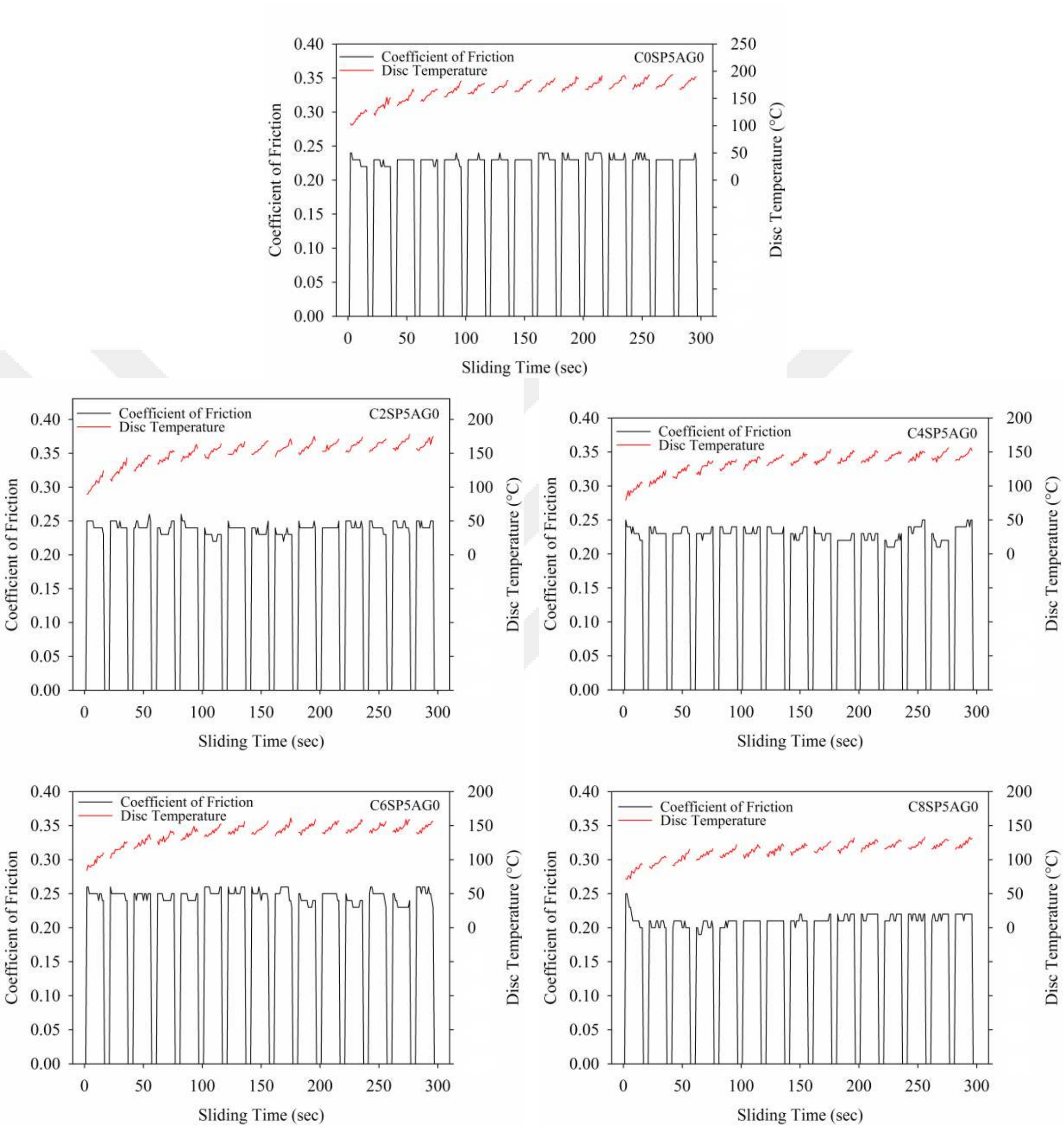

Figure 3. 8 Evolution of the coefficient of friction of SP5 samples with various CNSL ratios.

In the case of composites with 20 wt. % of SP, as shown in Figure 3.9, the effect CNSL content on the friction coefficient is more pronounced especially for samples containing 6 wt. % and 8 wt. % of CNSL.

Moreover, an instability is observed in the case of composites with 0 wt. % and 2 wt. % of CNSL. In general, the decrease in friction coefficient makes friction more stable. Disc temperatures also exhibit a similar pattern, rising up to a maximum of 145 °C.

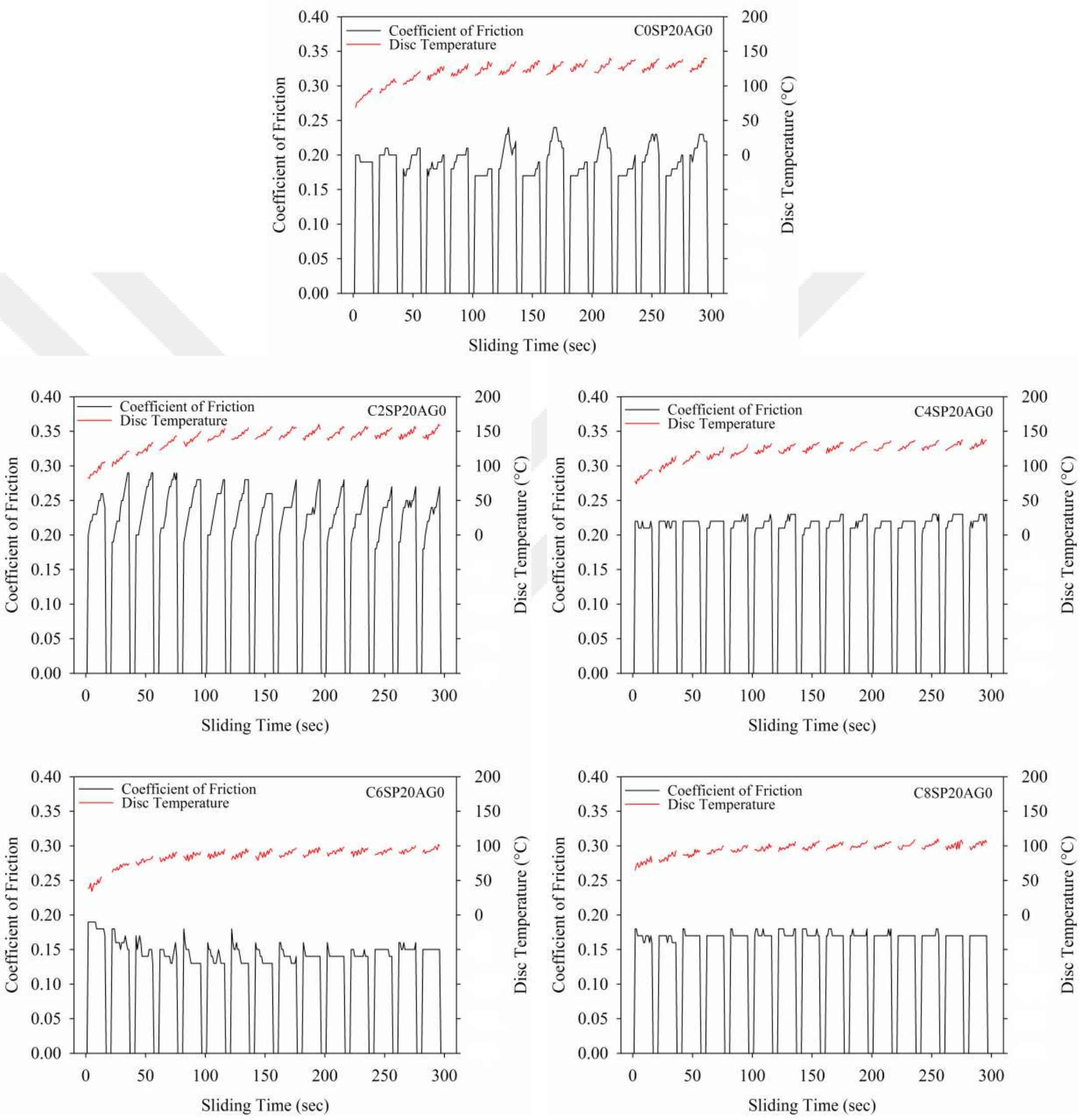

Figure 3. 9 Evolution of the coefficient of friction of SP20 samples with various CNSL ratios.

In the case of AG1 samples, the increase of CNSL content implies much more stable friction cycles (compared to samples with SP) with a slight decrease of the friction coefficient. Besides, the presence of AG induces a decrease of the disc temperature.

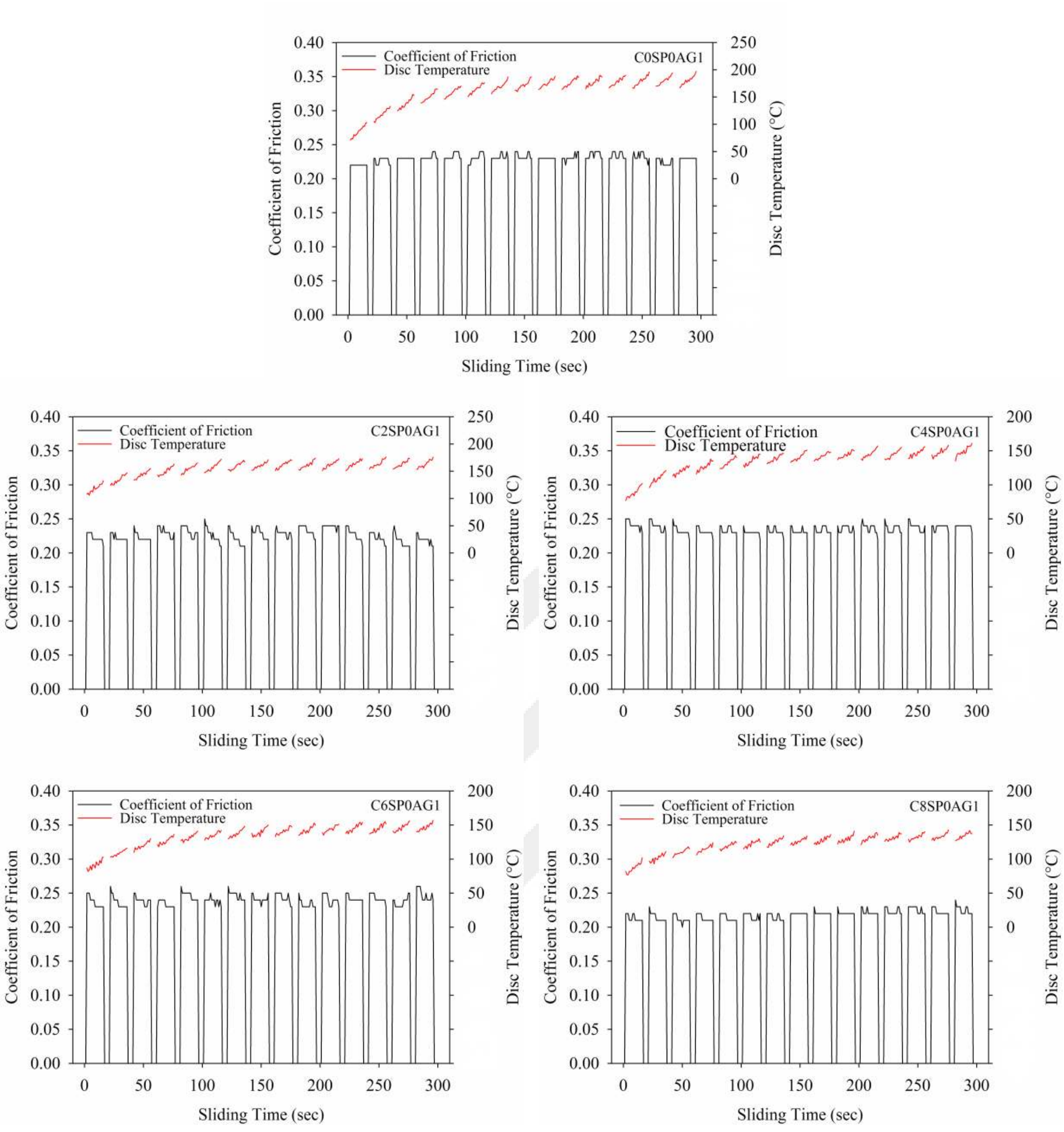

Figure 3. 10 Evolution of the coefficient of friction of AG1 samples with various CNSL ratios.

Figure 3.11 illustrates the evolution of the friction coefficient and the disc temperature for AG4 samples. A similar trend as AG1 samples is observed in the case of AG4 samples.

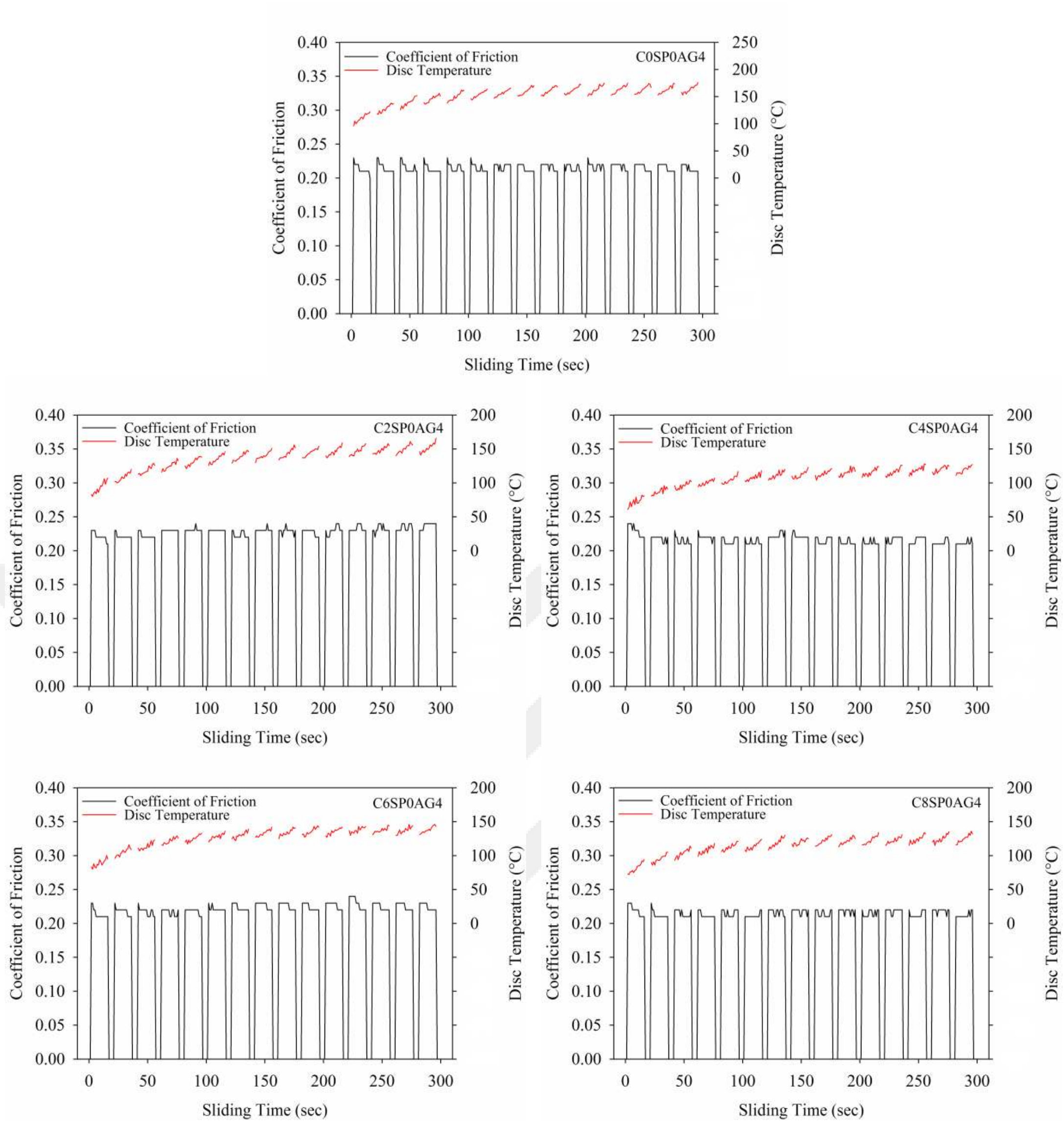

Figure 3. 11 Evolution of the coefficient of friction of AG4 samples with various CNSL ratios.

3.1.5 Effect on the Average Friction Coefficient

The effect of CNSL content on the average friction coefficient of composites containing sepiolite clay is presented in Figure 3.12. No significant effect is observed for samples without SP (SP0) and samples with 5 wt. % of SP. However, in the case of samples containing 20 wt. % of SP, for CNSL contents of 6 wt. % and 8 wt. %, a significant decrease in the average friction coefficient is observed. These results are in correlation with the literature. Yanar et al. who investigated the effect of CNSL content on the tribological properties observed a dramaticly decrease of the friction coefficient for CNSL ratios 1 wt. %, 2 wt. % [30].

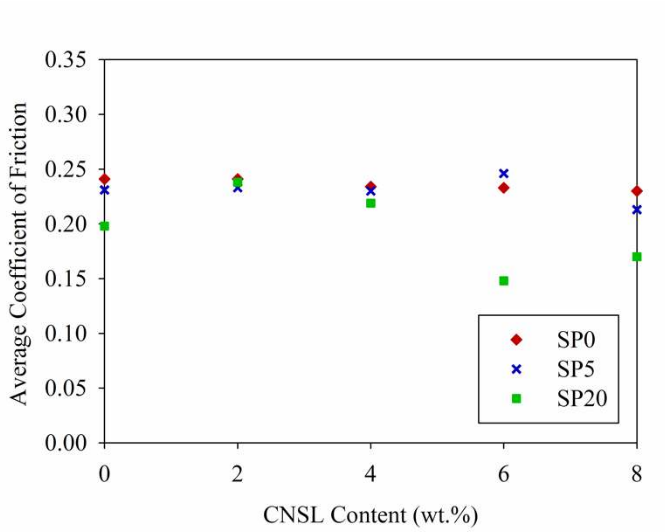

Figure 3. 12 Average coefficient of friction of sepiolite clay containing samples with various CNSL ratios.

The results obtained with samples containing silica aerogel are presented in Figure 3.13. This Figure shows that the CNSL ratio does not have a significant effect on the average friction coefficients which are approximately similar in the whole range of CNSL contents.

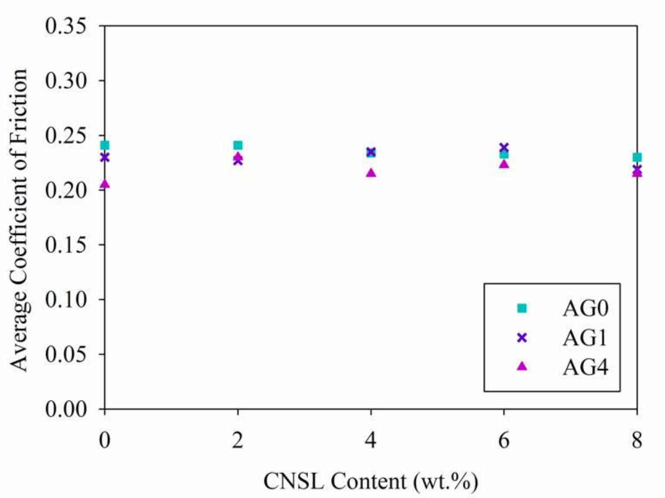

Figure 3. 13 Average coefficient of friction of silica aerogel containing samples with various CNSL ratios.

3.1.6 Effect on Wear Properties

3.1.6.1 Specific Wear Rate

Figure 3.14 presents the effect of various CNSL contents on the specific wear rate of composite filled with 5 wt. % and 20 wt. % of SP. According to this figure, for samples without SP (SP0), the specific wear rate decreases with CNSL amounts higher than 4 wt. %. Although samples with 5 wt. % of SP seem to follow the same evolution as SP0 samples except at a CNSL content of 4 wt. %, it seems difficult to draw a conclusion for samples with 20 wt. % of SP. In that case, the highest specific wear rate was measured at 2 wt. % of CNSL and the lowest one at 4 wt. % CNSL. Interestingly, for SP20 samples, these results are in correlation with the evolution of the porosity (discussed in section 3.1.2) which decreases until 4 wt. % of CNSL and stabilizes (see Figure 3.3). Moreover, the Shore D hardness of these samples increases until 4 wt. % of CNSL and stabilizes (see Figure 3.5 and discussions in section 3.1.3). Therefore, it can be concluded that from 4 wt. % of CNSL, as the porosity is stabilized, the maximum compaction of the fillers and thus, a high level of interactions between SP fibers and the resin is reached and the voids between the fillers is stabilized. This induces a stabilization of the hardness to the highest and constant value. Consequently, it is not surprising that the specific wear rate reaches its lowest values and stabilizes above 4 wt. % of CNSL.

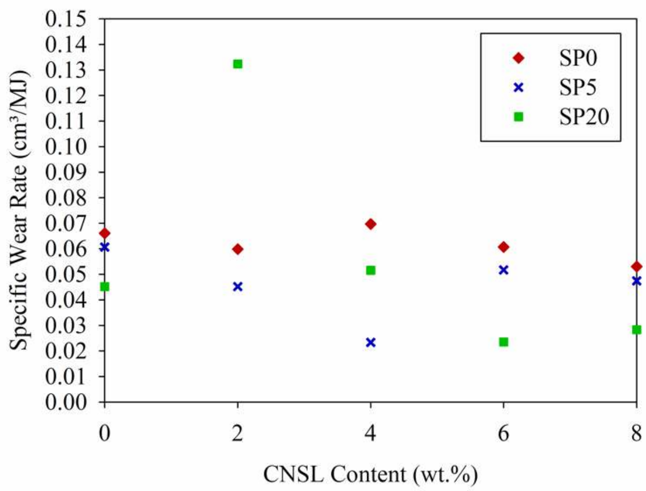

Figure 3. 14 Specific wear rate of sepiolite clay containing samples with various CNSL ratios.

Concerning samples containing silica aerogel, Figure 3.15 shows that the increase in CNSL slightly decreases the specific wear rate for samples without silica aerogel (AG0 samples). This trend is more pronounced for samples containing AG.

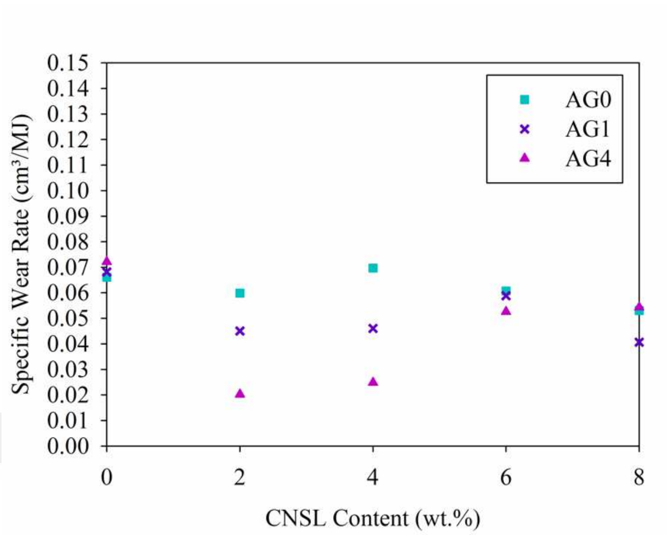

Figure 3. 15 Specific wear rate of silica aerogel containing samples with various CNSL ratios.

3.1.6.2 Wear Mechanism

The SEM micrographs of worn SP5 and SP20 samples containing various amounts of CNSL are presented in Figure 3.16. The pictures related to SP5 samples show that when the CNSL content increases from 0 to 4 wt. %, several plateaus with decreasing sizes appear. It should be noticed that, as shown in Figure 3.14, the specific wear rate of those samples decreases and reaches its lowest value for the sample with 4 wt. % of CNSL. This decreasing trend is also observed in the size of the plateaus on pictures C0SP5AG0, C2SP5AG0 and C4SP5AG0 where only the CNSL amount increases. Therefore, these plateaus can be qualified as secondary plateaus.

When pictures related to SP20 samples are considered, there are no secondary plateaus for composites with 6 wt. % and 8 wt. % of CNSL. These results are in correlation with the low specific wear rates observed in Figure 3.14 for these samples.

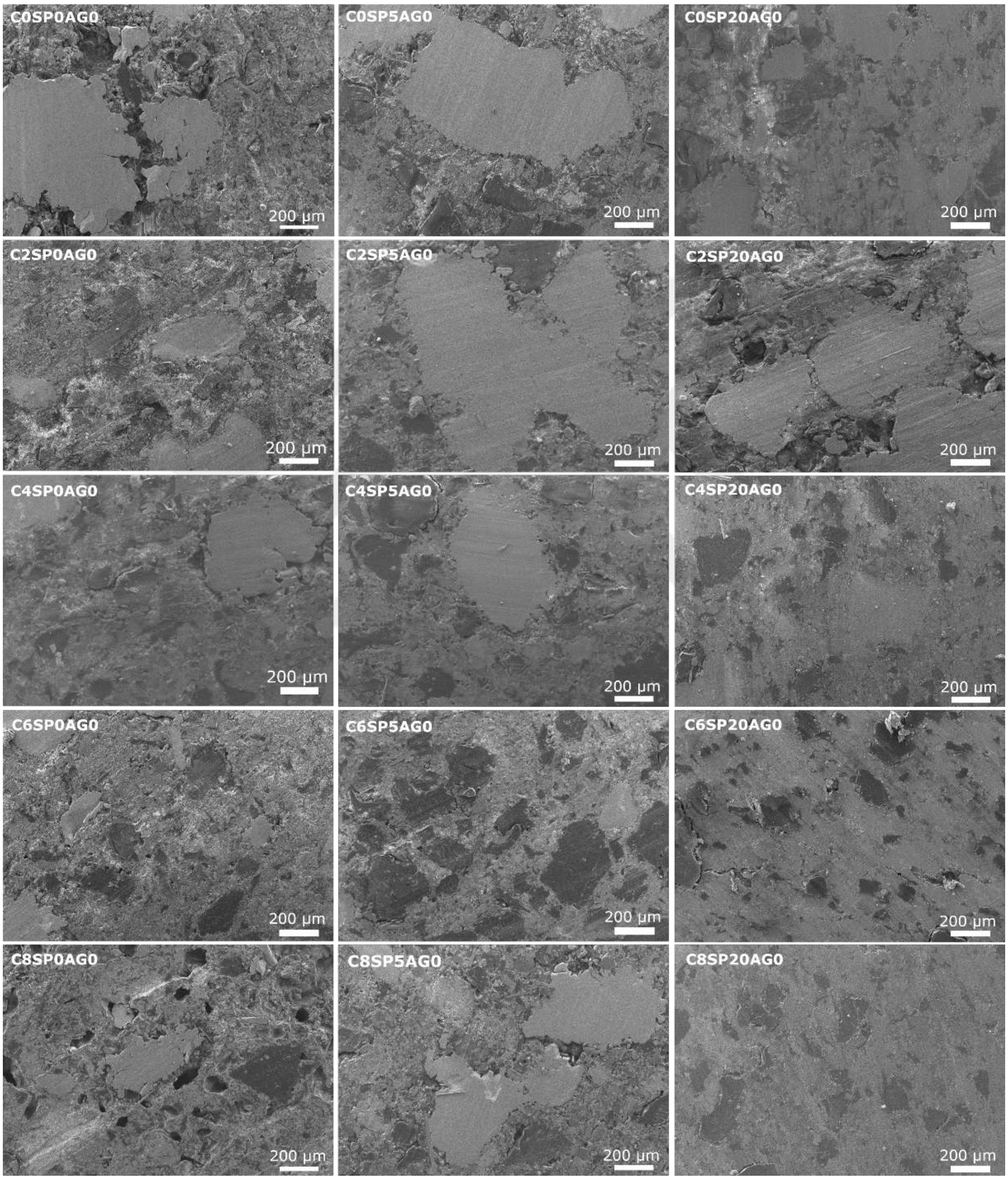

Figure 3. 16 SEM micrographs of worn SP5 and SP20 samples containing various amounts of CNSL.

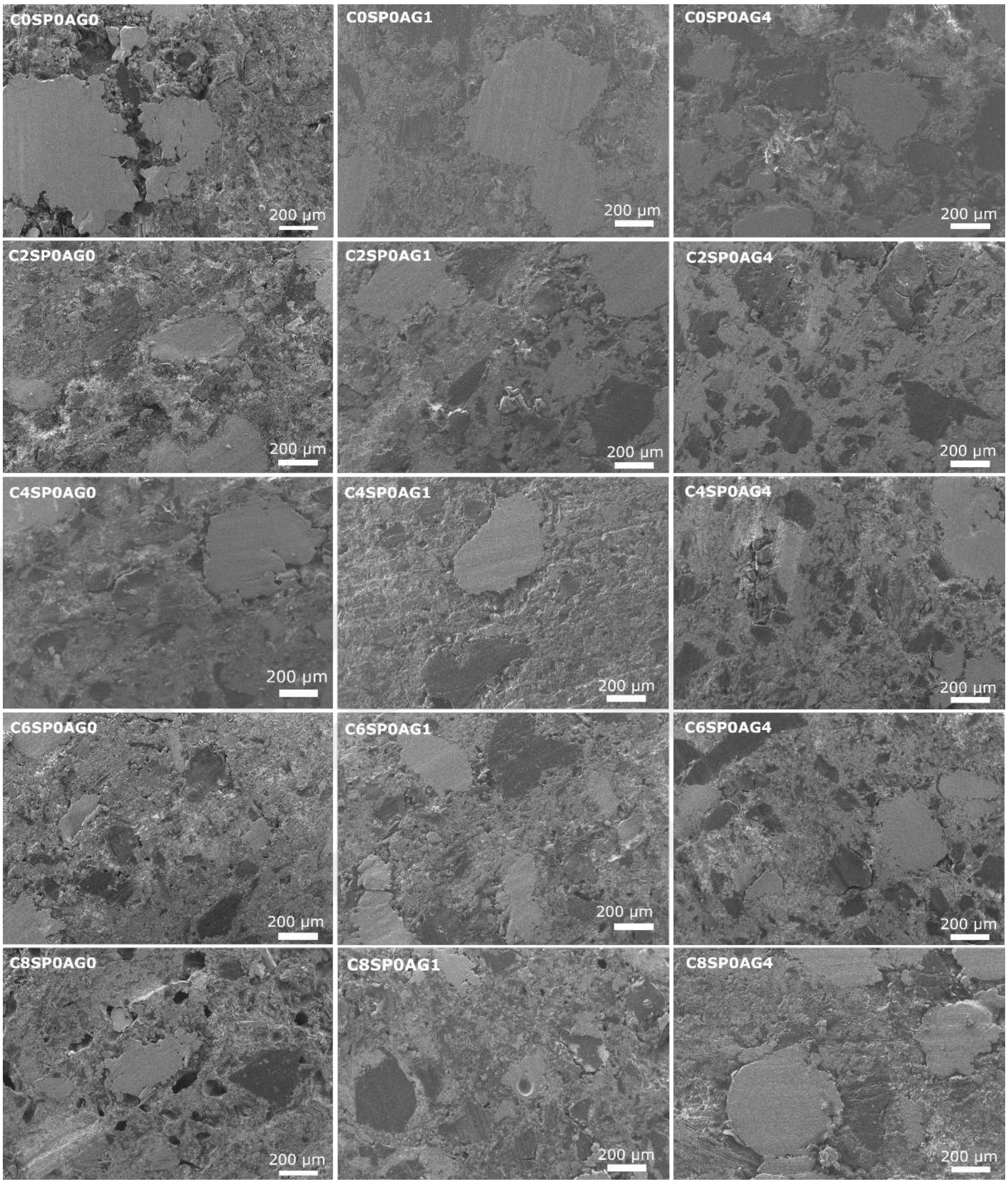

Figure 3. 17 SEM micrographs of worn AG1 and AG4 samples containing various amounts of CNSL.

The SEM micrographs of worn AG1 and AG4 samples containing various amounts of CNSL are presented in Figure 3.17. In the case of AG1 samples, similarly to samples containing sepiolite clay, when the specific wear rate is high (see Figure 3.15), secondary plateaus are observed such as the case in Picture C0SP0AG1.

In the case of AG4 samples, the lowest specific wear rate is observed for the sample with 2 wt. % of CNSL (Figure 3.15) which induces a surface with almost no plateau as shown on Picture C2SP0AG4.

The aim of this section was to determine the optimum CNSL ratio that provides suitable properties for organic brake pads composites. The main parameters important for friction materials, such as the density, the hardness, the porosity, the friction coefficient, and the wear rate were investigated. The friction stability and the amount of wear have a major influence in determining the optimum CNSL ratio. Relatively stable friction evolutions and lower wear rate were observed at 4 wt. % CNSL content for both sepiolite clay and silica aerogel containing composites.

Therefore, in the following two sections, samples with a CNSL content of 4 wt. % and various amounts of SP or AG were prepared and characterized in order to investigate the effects of the filler content in both cases.

3.2 Effect of Sepiolite Clay Content on the Different Properties at the Optimum CNSL Content

3.2.1 Effect on the Density

In Figure 3.18, the effect of the increase of the amount of sepiolite clay on the density of composites containing 4 wt. % of CNSL is examined. It is clear that the increase in the amount of SP causes a decrease in the density of the material. While the density of the composition without SP is 2.21 g/cm^3, when the sepiolite ratio increases until 20 wt. %, the density decreases until 2.11 g/cm^3.

This may be due to the fact that the raw materials in the composition cannot be fully wetted by the CNSL, as a result of the increase in the amount of SP, the raw composition is not compacted sufficiently. In addition, the decrease in the bulk density of the raw compound explains the decrease in the ultimate density, since the increase in sepiolite is compensated by barium sulphate with a higher density than the sepiolite.

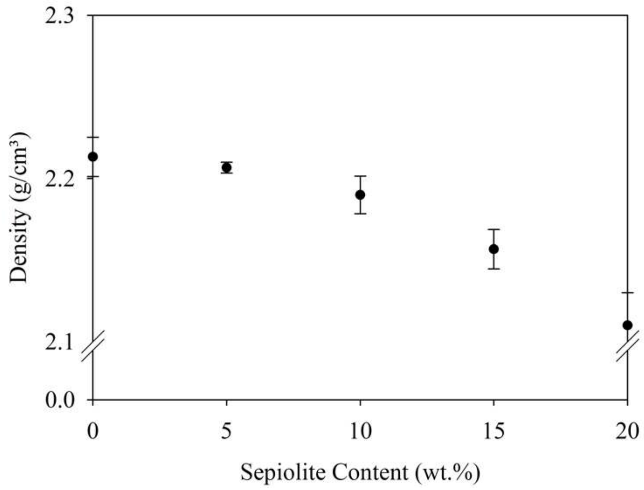

Figure 3. 18 Density of sepiolite clay containing samples.

3.2.2 Effect on the Porosity

Figure 3.19 illustrates the effect of different amounts of sepiolite clay on the porosity. It can be seen that the increase in the amount of SP induces a decrease of the porosity up to 10% and then it stabilizes around 1.5%. While the highest porosity value is 2.3%, the lowest porosity value is 1.5%. As the density decreases with the increase of SP content, an increase in porosity can be anticipated until 10 wt. % of SP.

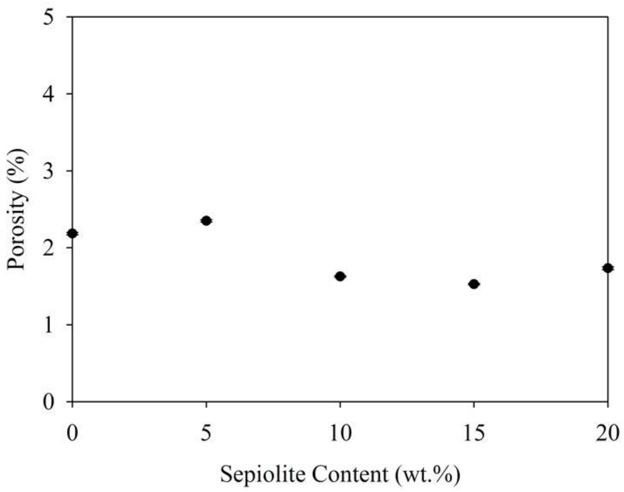

Figure 3. 19 Porosity of sepiolite clay containing samples.

3.2.3 Effect on Shore D Hardness

Figure 3.20 illustrates the effect of different amounts of sepiolite clay on the shore D hardness of the sample. This figure clearly shows that the increase of the amount of SP causes the rise of the hardness of the composites. The shore D hardness was 85 for the sample without SP while the hardness increased to 90 at the maximum sepiolite ratio.

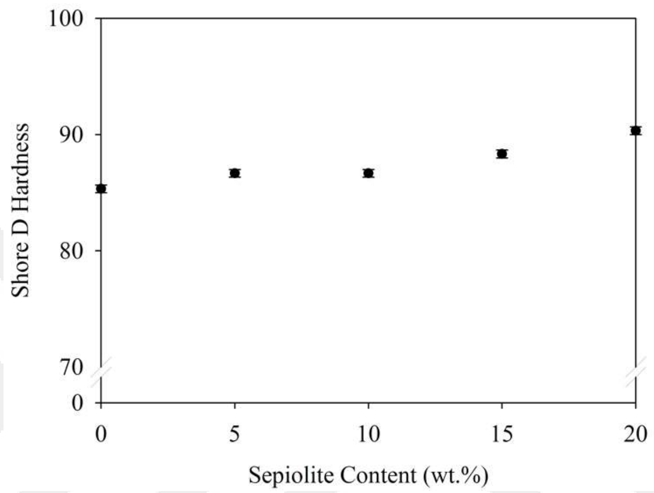

Figure 3. 20 Shore D hardness of sepiolite clay containing samples.

3.2.4 Evolution of the Friction Coefficient with Sliding Time

Figure 3.21 shows the effect of different ratios of sepiolite clay on the evolution of the friction coefficient. According to Figure 3.21, relatively similar friction curves were obtained with the increase of the amount of sepiolite clay. Nevertheless, in the case of the composite with 20 wt. % of sepiolite clay, the evolution of the friction coefficient is smoother and more stable in each braking period.

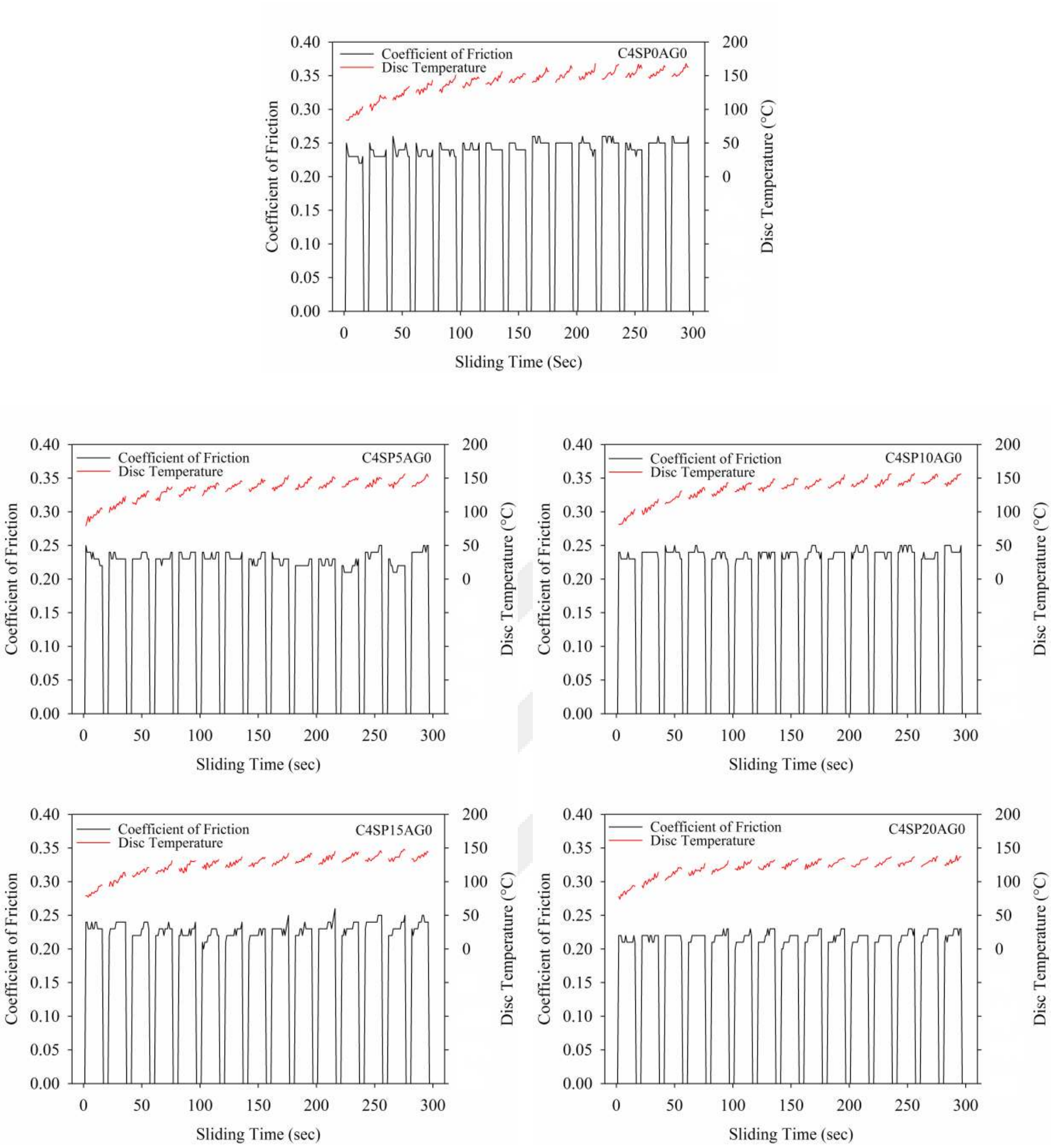

Figure 3. 21 Evolution of coefficient of friction of sepiolite clay containing samples.

3.2.5 Effect on Average Friction Coefficient

Figure 3.22 shows the effect of the amount of sepiolite clay on the average friction coefficient. The average coefficient of friction varies between 0.24 to the lowest 0.22. It exhibited a deviation of less than 10%. Actually, no specific trend emerges concerning the effect of SP content on the average friction coefficient.

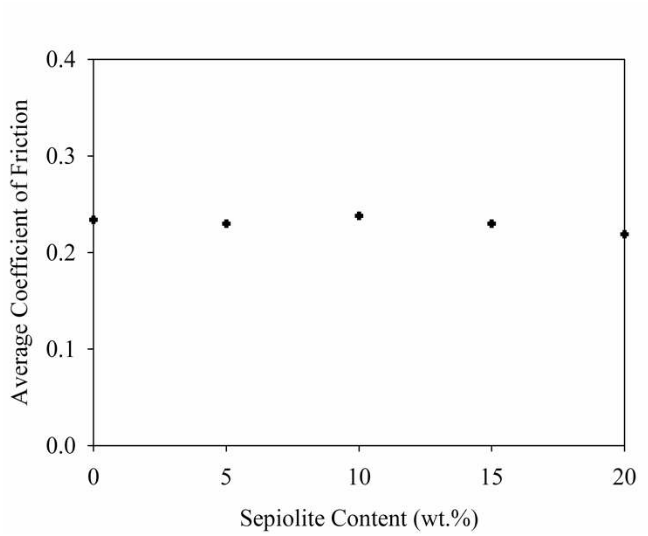

Figure 3. 22 Average coefficient of friction of sepiolite clay containing samples.

3.2.6 Effect on Wear Properties

3.2.6.1 Specific Wear Rate

Figure 3.23 shows the effect of sepiolite clay content on the specific wear rate. Initially, the addition of 5 wt. % sepiolite seems to reduce the amount of specific wear rate significantly, but as the SP ratio increases, the specific wear rate increases. However, compared to the base composition 20 wt. % sepiolite has a lower specific wear rate.

At a first glance, one can think that the decrease in specific wear rate is due to the decrease in the amount of barite in the case of the sample with 5 wt. % of sepiolite clay. However, as the amount of SP increases, the specific wear rate increases. Therefore, variations occurring in the specific wear rate cannot be attributed to the barite content.

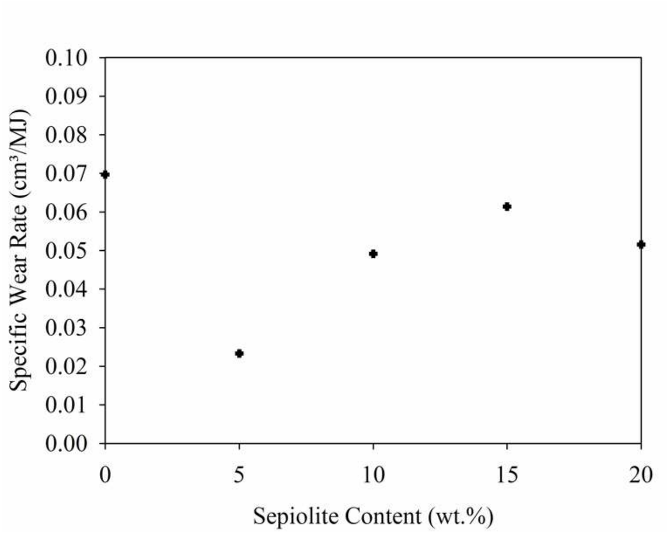

Figure 3. 23 Specific wear rate of sepiolite clay containing samples.

3.2.6.2 Wear Mechanism

As shown on Figure 3.24, for compositons with 4 wt. % of CNSL and various contents of sepiolite clay (5, 10, 15, 20 wt. %), the mechanism of the wear follows the same tendency as the cases described in the previous section. A decrease of the size of secondary plateaus related to a decrease in the specific wear rate (Figure 3.23) is observed.

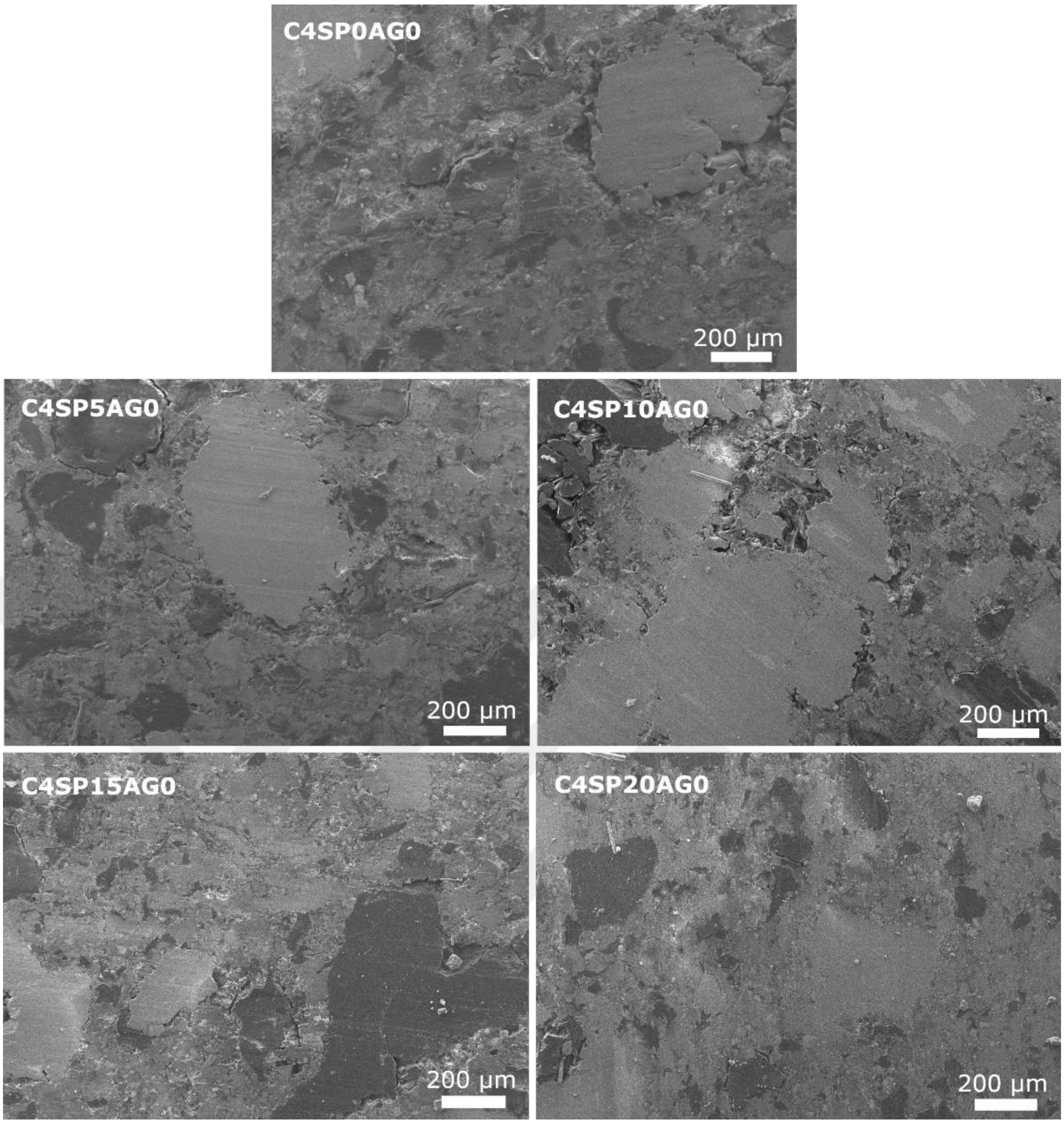

Figure 3. 24 SEM micrographs of worn samples containing 4 wt. % of CNSL and 0, 5, 10, 15 and 20 wt. % of SP.

3.3 Effect of Silica Aerogel Content on the Different Properties at the Optimum CNSL Content

3.3.1 Effect on the Density

Figure 3.25 shows the effect of silica aerogel content on the density of the composites. It can be seen that the different AG amounts do not have a significant effect on the density. While the highest density value was measured as 2.21 g/cm^3 for the composition without AG, the lowest density value of 2.12 g/cm^3 was measured at both 0.46 wt. % and 1.39 wt. %.

No significant effect on density was observed probably due to the much lower amount of aerogel used compared to the sepiolite filler. Also, the hydrophobic properties of silica aerogel may have affected the compressibility of the mixture by affecting the wetting behavior.

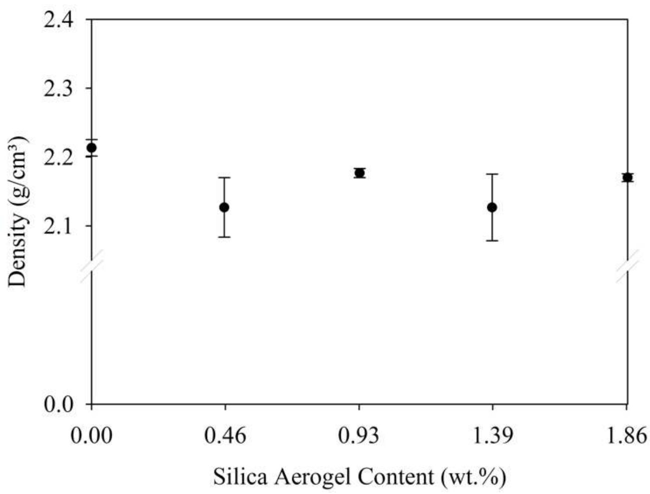

Figure 3. 25 Density of silica aerogel containing samples.

3.3.2 Effect on the Porosity

Figure 3.26 shows the effect of silica aerogel filler on the porosity of the composites. Although a sinusoidal evolution is observed. Actually, an increasing general trend can be noticed.

The increase of the porosity with the addition of aerogel can be explained by the morphology of the aerogel. It may have increased the porosity ratio of the mixture due to its porous structure.

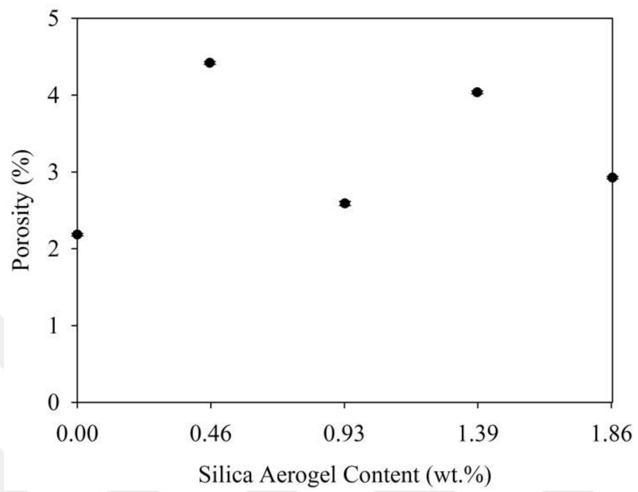

Figure 3. 26 Porosity of silica aerogel containing samples.

3.3.3 Effect on Shore D Hardness

Figure 3.27 shows the effect of silica aerogel filler on Shore D hardness. According to this figure, the Shore D hardness decreases almost linearly with the increase of AG content. This evolution can be attributed to the porous structure of the aerogel.

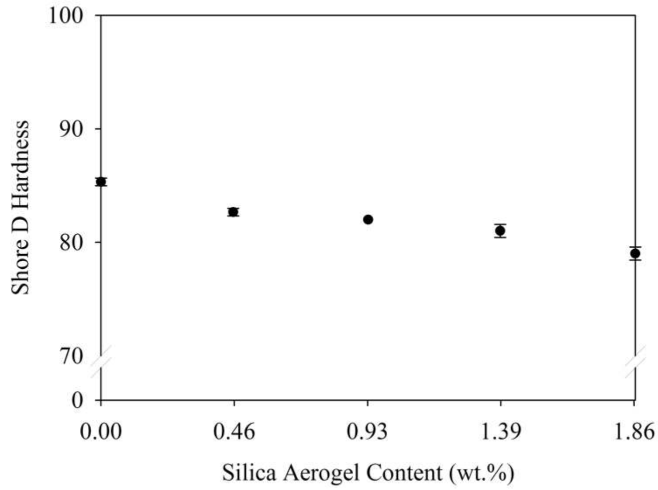

Figure 3. 27 Shore D hardness of silica aerogel containing samples.

3.3.4 Evolution of the Friction Coefficient with Sliding Time

According to Figure 3.28 AG filler appears to make the development of friction more stable. The most stable graphic was obtained with the use of 1.39 wt. % of AG (AG3). In addition, when the disk temperatures of the AG added compositions are compared, there is a difference of 17 °C between the AG0 and AG3 composites, which have the same friction coefficients. The composition with AG filler appears to lesser increase the disc temperature.

Likewise, there is a 16 °C temperature difference between the AG2 and AG4 composites which have the same friction coefficients. It was observed that the increase in the amount of AG decreases the disc temperature.

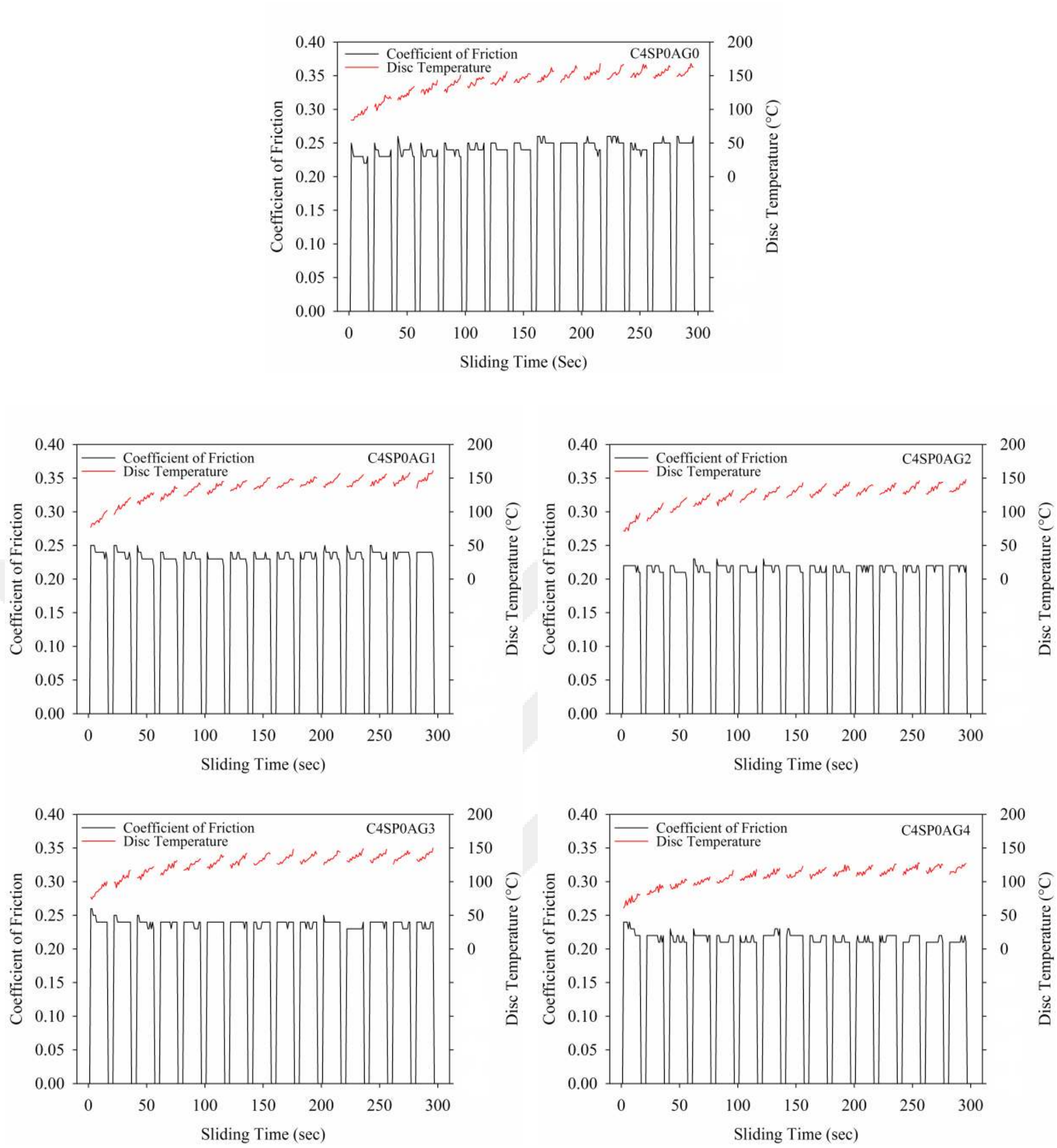

Figure 3. 28 Evolution of coefficient of friction of silica aerogel containing samples.

3.3.5 Effect on the Average Friction Coefficient

Figure 3.29 shows the evolution of the average friction coefficient of the samples with an increasing amount of AG. It can beseen that the coefficient of friction of the composites decreases from 0.23 to 0.21 by 0.93 wt. % and 1.86 wt. %.

The highest percentage of aerogel, 1.86 wt. %, and the average friction coefficient of the composition without aerogel are the same as 0.23.

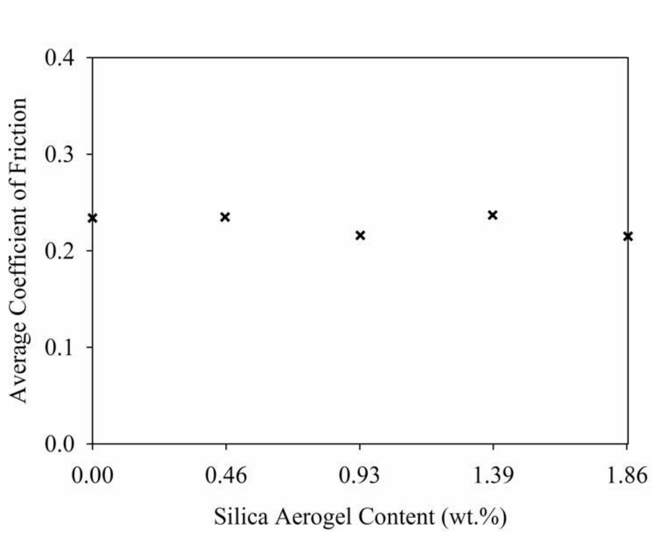

Figure 3. 29 Average coefficient of friction of silica aerogel containing samples.

3.3.6 Effect on Wear Properties

3.3.6.1 Specific Wear Rate

Figure 3.30 shows the changes in the specific wear rates as a function of the AG content. According to this figure, for all samples filled with AG, the specific wear rate is lower than the composites without silica aerogel. Although the wear is increased by 1.39 wt. %, the increase in the AG3 composite, which has a lower wear amount than the composite without AG, can be explained by the disc temperatures. The evolution ofthe disc temperature presented in Figure 3.31 clearly shows that the wear behavior is closely related to the temperature of the disc.

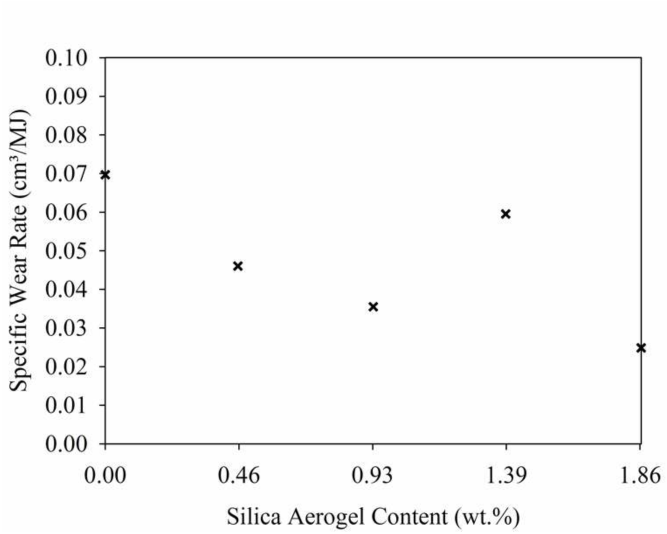

Figure 3. 30 Specific wear rate of silica aerogel containing samples.

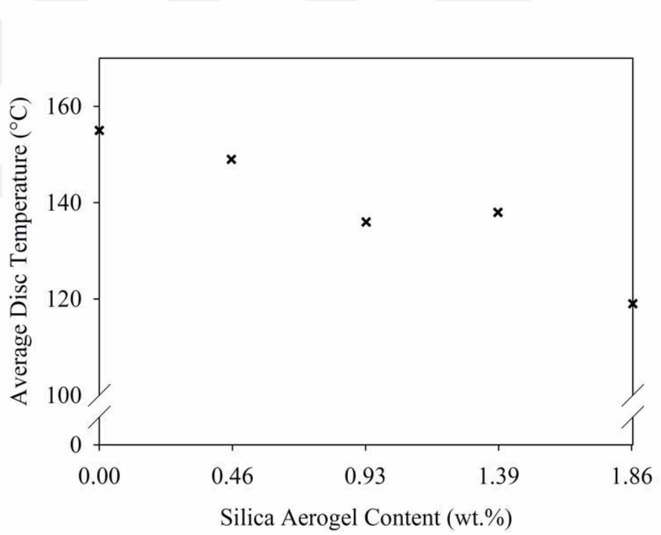

Figure 3. 31 Average disc temperature of silica aerogel containing samples.

3.3.6.2 Wear Mechanism

Figure 3.32 illustrates the results obtained for samples containing 4 wt. % of CNSL with various silica aerogel ratios (AG1, AG2, AG3 and AG4).

According to Figure 3.30, the highest specific wear rate was observed for the composition with 1.39 wt. % (AG3). Its consequences on the worn surface of C4SP0AG3 (Figure 3.32) is the apparition of disintegrated particles.

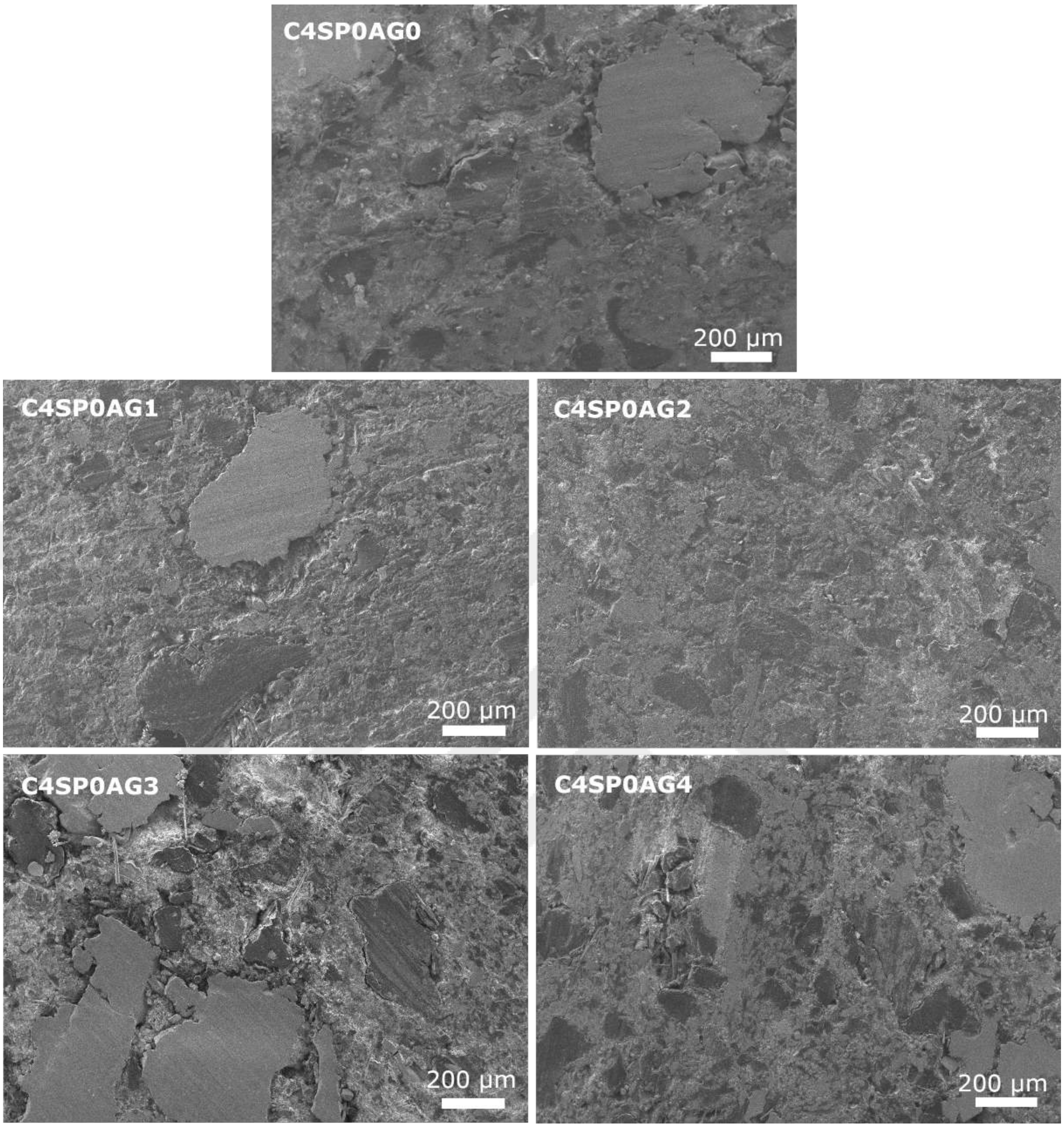

Figure 3. 32 SEM micrographs of worn samples containing 4 wt. % of CNSL and increasing content of AG.

CHAPTER 4

CONCLUSIONS

Main conclusions on the contribution of sepiolite clay and silica aerogel with various CNSL ratio on the physical properties and friction, wear behavior of the brake pads as a friction material could be summarized as follows:

Effect of CNSL:

It was observed that the density of both SP and AG containing compositions increased with the increase of CNSL content. However, it was observed that the porosity ratio decreased.

Although the Shore D hardness differs according to the filler used, it was observed that the Shore D hardness decreased with the increase of CNSL content in general. Except for 20 wt. % SP composition both additives did not appear to have a significant effect on friction behavior.

Moreover, it was observed that the highest coefficient of friction value was 0.24 and the lowest one was 0.20 for AG containing samples while the highest coefficient of friction value was 0.24, and the lowest one was 0.14 in the compositions containing SP.

Relatively lower coefficient of friction values occurred in compositions with 6 wt. % and 8 wt. % of CNSL with SP filler.

It was determined that CNSL has a reducing effect on wear. The lowest wear values were obtained with a content of 4 wt. % of CNSL for SP filled composites and 2 wt. % of CNSL for AG filled ones.

Effect of sepiolite clay:

It was observed that SP filler has a reducing effect on density. Despite the decrease in density, the porosity first increased and then decreased for samples with 5 wt. % of SP, and then decreased again with the increase in the SP content.

Besides, the SP filler significantly increased the shore D hardness of the composites.

It was seen that the SP containing samples have a lower wear value than the samples without SP or AG in all SP contents and a lowest wear value of 0.023 cm^3/MJ was obtained with SP5.

Effect of silica aerogel:

Similarly to SP, the AG filler was found to reduce the density. However, unlike sepiolite clay, it was observed that AG filler increased the porosity.
It was also observed that the AG filler significantly reduced the shore D hardness of the material. Besides, the AG containing compositions showed a more stable friction pattern. Similarly to SP containing composites, the average friction coefficient resulted close to the compositions without AG in all ratio.
The AG filler provides a lower wear rate than the compositions without AG in all ratios, and a lowest wear rate of 0.024 cm^3/MJ was obtained for AG4.

In view of all these results, it can concluded that SP filler provides an increase in the strength without adversely affecting the wear behavior in brake pad composites. Similar conclusions can be drawn with AG filler which provides a more stable friction behavior and a low wear rate.

To conclude, in terms of friction and wear properties, the optimal results were obtained for SP5 and AG4 composites with CNSL content of 4 wt. %. According to the standard recommended by the Society of Automotive Engineers (SAE – J866) on ‘Friction Coefficient Identification and Environmental Marking System for Brake Linings’, the composites optimized in this study can be classified as D class friction materials as their coefficient of friction is located between 0.15 and 0.25.

Perspectives

As AG provides a more stable friction patterns, the effect of this filler on properties such as noise, vibration, harshness (NVH) of organic brake pad composites can be investigated in the future.

In addition, the synergistic effect of 5 wt. % SP and AG4 with a CNSL content of 4 wt. % where optimum results are obtained, may be a subject of research in the future.

As a result, it has been shown that SP and AG fillers can be used to improve the friction and wear properties of organic brake pad composites.

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