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A THESIS FOR THE DEGREE OF MASTER SCIENCE

**Performance characteristics of a modified brake
pad manufactured with lignin polymers
as binder and filler materials**

리그닌을 함유하는 친환경 브레이크패드의 마찰특성 연구

by Jeesu Park

PROGRAM IN ENVIRONMENTAL MATERIALS SCIENCE

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Abstract

Performance characteristics of a modified brake pad manufactured with lignin polymers as binder and filler materials

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The development of environmentally-friendly brake pads manufactured with several technical lignins such as soda lignin (SL), sulfuric acid lignin (SAL) and heat-treated SAL (HL) as frictional material is presented in this study. Research was carried out with a view to exploiting the characteristics of the lignin, which is largely deposited as waste, in replacing phenol formaldehyde resin (PR, binder) and cashew nut shell liquid (CNSL, filler) which are costly and known to cause environmental pollution. The amount of lignin added to the modified brake pad ranged up to 40 wt% of the total weight ratio of PR and CNSL respectively, while the contents of the other ingredients were fixed. The performance characteristics of the modified brake pads were evaluated and compared using several tests.

The results showed that all of the lignin-based brake pads adhered to the SAE standard (0.25) for friction coefficient, which is the primary contributor to the performance of a braking system. In particular, the replacement of PR

with SL demonstrated a better friction coefficient than did replacement with SAL or HL, reaching up to 0.6. In general, the performance of the samples decreased when the lignin content increased. However, 10% of lignin was determined to be a sufficiently suitable material for brake pads.

On the other hand, when lignin was used as filler with CNSL, HL-based brake pads showed a significant improvement in wear resistance of 0.12 g (dust generation) compared to SL and SAL-based brake pads, which had a resistance of approximately 0.25 g. As with the previous results, the results of every performance test decreased as lignin content increased. Brake pads containing 10% of HL were selected as the most suitable material for brake pads, as their performance most closely matched the commercial brake pad.

Key words: **Brake pad, Lignin, Friction, Binder, Phenol formaldehyde resin, Cashew nut shell liquid, Wear resistance, Filler**

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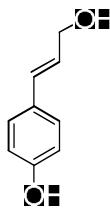
1. Introduction

1.1. Lignin

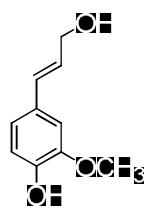
Lignin is a three-dimensional amorphous phenolic polymer composed of up to three different phenyl propane monomers, *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, as shown in Figure 1. These monomers are bonding each other with various inter-unit linkages such as β -O-4 (40-60%), α -O-4 (3-5%), biphenyl (3.5-25%), and β -5 (4-10%) (Brunow and Lundquist, 2010).

Lignin is binding the cells, fibers and vessels which constitute wood and the lignified elements of plants. It is a complex chemical compound, cross-linked polymer that forms a large molecular structure, reaching the range of 100,000 Daltons or even greater (Janshekar and Fiechter, 2005).

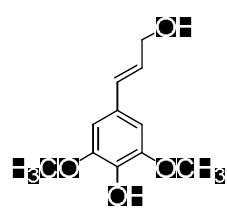
Lignin is formed by photosynthesis and makes up about 20~30% depending on the species, conferring mechanical strength to the cell wall which provides stiffness and rigidity. Beyond the mechanical strength function, lignin plays several other important biological roles in plants. For example, lignin is much less hydrophilic than cellulose and hemicelluloses, so it prevents the absorption of water by these polysaccharides in plant cell walls and also acts as an intercellular binder (Jung et al., 1993).



p-coumaryl alcohol



coniferyl alcohol



sinapyl alcohol

Figure 1. Three C6C3 types of monolignols (*p*-coumaryl, coniferyl, and sinapyl alcohol)

1.2. Overview of residual lignin from bio-refinery

Recently, lignocellulosic biomass (composed of lignin, cellulose and hemicellulose) has received significant attention as an important primary and renewable resource. With growing concern over depleting fossil resources and the rising amount of greenhouse gas emissions there is a high level of interest in eco-friendly products that originate from bio-renewable sources, including lignocellulosic materials. As such, many researchers have been working to find fields for the application of lignocellulosic biomass.

Among several applications, one development currently being expanded is the production of fuel ethanol from the cellulose contained in agricultural residues and waste wood (Huber et al., 2006). During the biochemical (bioethanol) conversion process, only cellulose and hemicellulosic fractions are converted into fermentable sugar, which resulted in a lot of residual lignin produced in the pretreatment and hydrolysis step. In addition, according to Kim et al., over 50 million tons of byproduct, namely, lignin, has been produced annually in the US pulping/paper industry (Kim et al., 2014). Because the bio-ethanol and pulping industries are well established, a large amount of lignin is generated from physical/chemical processes or technologies, converting biomass to renewable energy resources. However, only 2% of the available lignin is isolated and converted into value-added products, primarily in the formulation of dispersants, binders, fillers, surfactants and chemicals, while the rest is largely burned in the chemical recovery processes of the pulping and bio-ethanol manufacturing industries (Stewart, 2008).

As such, the development of value-added lignin-based products is

essential to maintaining the economic competitiveness of the bio-ethanol and pulping process. Total utilization of biomass will be the key to solving both the economic and the environmental challenges.

1.3. Applications and research trends in lignin

Several lignin applications have already been investigated earlier, but there still are limitations to the utilization of lignin as value-added products compared to the amount of lignin that occurs from pulping and bio-ethanol process. The following are examples of research in the area of lignin application that have been carried out thus far: (1) Carbon fibers- lignin can be used for carbon fibers through melt spinning and thermal treatments, (2) Phenolic compounds- phenolic compounds could be obtained through cleavage of various inter-unit linkages of lignin in sub/supercritical treatment, (3) Adhesives- lignin-based modifier (phenol formaldehyde resin, urea formaldehyde resin, etc.) may be used for panel boards such as plywood, hardboard and particleboards, (4) Plastic materials- lignin-based polymers can be used to produce plastic materials, for example, in the electronics industry and in concept cars, (5) Activated carbon- can be made from lignin and used for cleaning of environmentally hazardous emissions to air and water, (6) Rubber- lignin can be used as a natural filler in rubber to modify its characteristics (Olivares et al., 1988).

As mentioned above, lignin is a very complex biopolymer and contains a large number of phenolic OH groups. In addition, lignin has an aromatic and highly cross-linked structure, which is similar to the network of phenol formaldehyde resins (PR) and cashew nut shell liquid (CNSL). PR are polycondensation products of phenols and aldehydes, in particular phenol and formaldehyde. They are used in/for cast (engine manufacturing and molding), wheels (grinding wheels), abrasive cloth, felt (car interior) and friction material (brake pads) industries. CNSL is a by-product that is generated from the cashew industry. The cashew nut has a shell of about 1/8 inch thickness,

which is a honeycomb structure containing a dark viscous liquid called CNSL. This is a source of naturally occurring phenols, which are composed of anacardic acid, cardol and cardanol. CNSL has innumerable applications, such as friction materials, paints, laminating resins, rubber compound and intermediates for chemical industries (Bisanda and Ansell, 1992).

Among both PR and CNSL applications, the demand of the brake pad market is the most remarkable field. In brake pads, PR acts as a binding agent for gluing other friction components together, and CNSL is used as filler to provide structural reinforcement, which offers high strength and is extremely resistant to moisture, and gives excellent temperature stability. However, PR can be very expensive due to the fluctuating price of phenol. In addition, PR are toxic, and some are known as carcinogenic to humans, making them one of the most harmful pollutants in effluent discharge from diverse industries, which have caused severe environmental troubles (Donmez et al., 2008). Similarly, as demand for CNSL as a new material for brake pads increases, prices are also rising rapidly according to the demand (Murthy et al., 1979).

To overcome these problems, various alternate materials have been developed and investigated. However, there still are few materials which meet the demand, and improvements are needed. Therefore, in this study, three different types of lignin as new friction materials are tested and compared in order to reduce the environmental impact and improve cost effectiveness.

1.4. Objective

Traditionally, lignin has been viewed as a waste material or a low value by-product. Yet despite the high amount of residual lignin generated, there has been a lack of research into its application. As stated above, only 2% of residual lignin has been converted to value-added products (Stewart, 2008). For this reason, it is essential to focus on its possible applications.

During the last several decades, a lot of research has been carried out in the area of brake pad material development. Brake pad material should maintain a relatively high, stable and reliable friction coefficient under a wide range of braking conditions. A change in the friction coefficient is highly dependent on the components of brake pad materials and braking conditions (Eriksson and Jacobson, 2000). As a result, the brake pad industry has seen the birth of different brake pads in the past decade, each with their own unique composition, yet performing the very same task and claiming to be better than others. Brake pads generally consist of PR as a binder and CNSL as filler with several other ingredients. The use of PR and CNSL, however, has recently been avoided due to their environmental impact and a sharp increase in price.

For this reason, research all over the world today is focusing on ways of utilizing either industrial or agricultural wastes as a source of raw materials in the high performance materials and components industry. It is clear that there is a need to develop new material that can replace PR and CNSL as a brake pad component while maintaining the required performance levels (Calvo-Flores and Dobado, 2010).

According to the trends of the research, the purpose of this study was to develop a new modified brake pad using industrial waste (lignin). As lignin is

a readily available, very cheap and eco-friendly material, it was suitable as a brake pad material. It was found that lignin types and characteristics are different from various isolation protocol and biomass sources (Guerra et al., 2006). Therefore, in this study, three different types of lignin such as Soda, Sulfuric acid and Heat-treated sulfuric acid lignins, were characterized using several analytical methods in order to evaluate and compare their suitability for incorporation into PR as a binder and CNSL as a filler. In addition, the brake performance characteristics of modified brake pads produced with different component ratios (0~40%) of lignin were identified by friction coefficient, wear resistance, Izod impact strength and thickness swelling in water, and then the performance of each was compared according to the types and component ratios of lignin.

2. Theoretical backgrounds

2.1. Overview of braking system

The braking system fulfills the function of decelerating or pulling up a moving vehicle. Specifically, it is a mechanical device that slows or stops a moving object and inhibits motion. Most commonly, brakes use the friction between two surfaces pressed together to prevent a moving object's motion. Figure 2 shows the driving condition and braking condition of a disc brake.

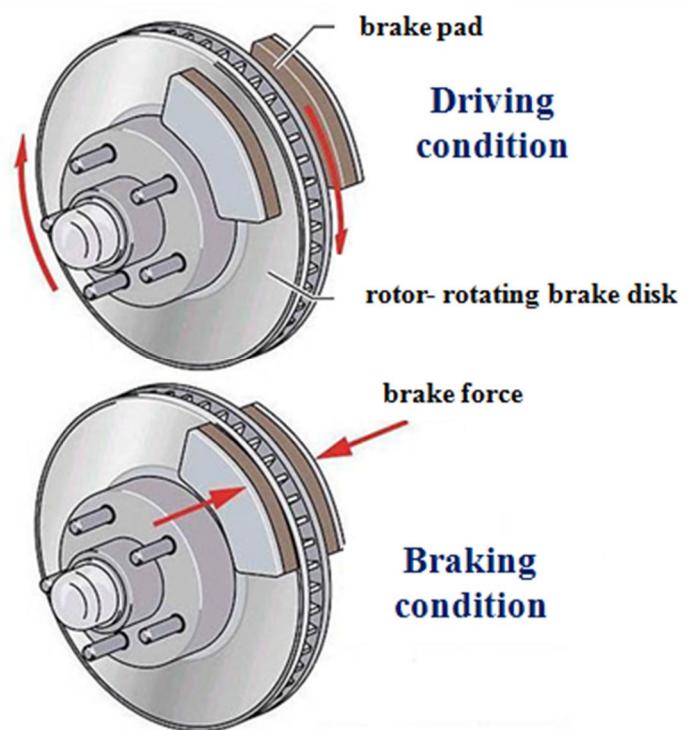


Figure 2. Disc brake system

2.1.1. Requirements of a brake system

The requirements of a brake system include but are not limited to the following: (1) There must be always sufficient braking action, and the brake must be guaranteed to work at the maximum speed and vehicle weight, (2) Reliability and durability shall be high, (3) It shall be simple to operate and not cause fatigue to the driver, (4) When a brake is not applied, it must not disturb the rotation of each wheel, (5) It shall be easy to check and to adjust.

2.1.2. Brake pads

A brake pad used for a disc brake system is installed at the brake caliper with its friction surfaces facing the rotor, which converts the kinetic energy of the moving object into thermal energy through friction. It is a part that plays the role of braking a rotating body by causing friction against the disc, a mating friction material. When the major parts are considered, the brake pad is composed of a friction material part that is actually in charge of friction and a back plate, which is a steel plate that transmits the pressure generated by a hydraulic cylinder. These two parts are bonded using adhesive. A wear indicating sensor, which indicates the wear limit, is attached to the back plate in order to prevent the possibility of the disc being damaged by direct friction between back plate and disc in the event that the wear of the friction material exceeds a certain limit.

A slot is drilled in the central part of friction material so that wear debris is smoothly discharged in order to suppress noise that may be produced in the event that wear debris produced due to friction is attached to contact surface. The opposite ends of friction materials are chamfered at a certain angle. These play a role in reducing brake vibration produced in contacting with mating

material before and after braking. A shim composed of rubber or a coated steel plate is attached between back plate and piston. This prevents the heat produced in braking from being transferred to a cylinder, and performs damping that suppresses noise produced due to vibration. Figure 3 is an image of a commercial brake pad.



Figure 3. Image of a commercial brake pad

2.2. Overview of friction material for brake pad

As stated above, a friction material is a material used for reducing power or stopping a moving object by converting the kinetic energy into thermal energy through friction. A friction material must meet the following requirements: its friction coefficient must be constant, there must be little change in braking force due to temperature, pressure, humidity, speed, and the like, its resistance to fade shall be excellent, its recovery shall be fast, its resistance to wear must be excellent, it must be heat resistant, its mechanical strength must be high, its contact surface must not be scored, the dimensional changes from the water and oil must be free to maintain the friction coefficient, as well as mass wear, and the feeling of braking must be excellent. Among these, the five most important characteristics that are considered when selecting a brake pad material are as follows: (1) Resistance to wear and constant friction coefficient at various operating conditions, (2) The effects of water or oil on brake's dimension change, (3) Thermal resistance, (4) Mechanical stiffness, (5) Impact strength.

2.2.1. Types of friction material

Looking at classification according to use, there are brake pads for brake systems for industrial machines, railway, and aircraft. There is also clutch facing for power train system, low-friction type for power train, and others.

In terms of classification according to material, there is asbestos friction material and non-asbestos friction material, which is an organic friction. There are also semi-metallic, low-steel, and non-steel friction materials, which are metallic friction materials. Looking at the category of inorganic friction

material, there is a sintered alloy for subway and rapid transit railway, and carbon composite material for aircraft and racing cars.

Looking at classification according to the ingredients of the friction material, there is binder, fiber, lubricant, abrasive and filler.

2.2.1.1. Binder

With regard to binder, which binds the ingredients that comprise a friction material, and which is used in order to maintain strength, resins, epoxy resins, PR, and the like, which are highly heat resistant thermosetting plastic, are used, as the use conditions of a friction material become harsh. Of these, PR, which has excellent heat resistance and formability, is mainly used. Binders have an effect on noise and wear characteristics in addition to strength.

2.2.1.2. Fiber

With regard to fiber, which maintains the shape of friction material and acts as a material that increases friction force, asbestos was generally used in the past. However, as its hazardousness to human health became an issue, its use became regulated. Accordingly, steel fiber, aramid fiber, glass fiber, copper fiber, and the like are used. Friction materials are classified according to the type and amount of applied fiber. Non-asbestos friction materials are classified into non-asbestos metallic friction material that contains metal and non-asbestos organic (NAO) friction material composed of nonferrous metal fiber and organic fiber only. Again, metallic friction materials are divided into

semi-metallic friction materials in which steel fiber content is 30% or more and low-metallic friction materials in which steel fiber content is 30% or less.

2.2.1.3. Lubricant

Lubricant reduces the wear of friction material and mating material, and prevents fine particulate matter emitted by friction from adhering to the rotor. In addition, lubricant plays a role in reducing the noise produced by the adhesion of two friction mating materials. Graphite, MoS₂, Sb₂S₃, ZnS, and the like are mixed and used.

2.2.1.4. Abrasive

Abrasive used for removing impurities attached to a rotor uses metallic oxide such as ZrSiO₄, Al₂O₃, SiO₂, and MgO, and has an effect on the increase of the friction coefficient. Using an abrasive makes it possible to maintain a continuous and constant friction coefficient over all temperature ranges by grasping the effective temperature range of the abrasive.

2.2.1.5. Filler

Filler is used in order to reduce costs by using low-priced raw materials, as well as to improve friction performance. Fillers include CNSL, rubber, and the like, which have the effect of reducing the wear rate at low temperatures, and inorganic fillers such as BaSO₄, CaCO₃, and Ca(OH)₂ which reduce the wear rate at high temperatures.

3. Literature review

3.1. Modified brake pad with various biomass

Stachowiak and Chan (2014) stated that safety and reliability are the main requirements for brake devices. As such, selecting the right materials for the friction brake elements (pads) is the most challenging task for brake system designers. In addition, Shibate et al. (1993) also mentioned that research into new friction materials for brake pads must be conducted due to recent environmental problems, as well as enhanced automobile quality requirements.

Therefore, Ibhadode and Dagwa (2008) investigated an eco-friendly material, a palm kernel shell (PKS) based brake pad. The brake pads were tested on a car for wear and effectiveness. When compared with a premium commercial brake pad, they were found to have performed satisfactorily. As such, the results suggested that palm kernel shell could be a possible replacement friction material.

Aigbodion et al. (2010) used bagasse as a friction material in brake pad, which is the residue remaining when sugar cane is pressed to extract the sugar. The bagasse was sieved into sieve grades of 100, 150, 250, 350 and 710 μm . The sieved bagasse was used in the production of brake pads in a ratio of 70% bagasse – 30% resin using compression molding. To investigate the properties of the brake pad, specific gravity, average wear, thickness swell in water, flame resistance test, compressive strength and hardness and brinell were tested. The results of this research indicated that the finer the sieve size, the better the properties. This is because the finer size composition showed a very

good dispersion, which led to a better interfacial bonding of the resin and the bagasse particles. The results obtained in this work were compared with the findings of commercial brake pads, which were in close agreement.

Bahari et al. (2012) determined the friction and heat resistance characteristics of automotive brake pads composed with different sizes (80 and 100 mesh) and percentages (10% and 30%) of coconut husk particle. The results showed that brake pads with 100 mesh and 10% composition of coconut husk particle showed the highest friction coefficient. For heat resistance, brake pads with 100 mesh and 30% composition of coconut husk dust showed the highest decomposition temperature, due to the high percentage of coconut husk particle in the composition, and thus increased the thermal stability.

The potential of using palm slag as a filler in brake pads was investigated by Ruzaidi et al. (2012). Different processing pressures (10~60 tons) were employed during the production of samples through compression molding. The properties examined included hardness, compressive strength, and wear behavior. The results showed that brake pad samples prepared with 60 tons of compression pressure resulted in the most desirable properties. This is because increasing the pressure will help the composite materials to pack and eliminate voids, keeping porosity to a minimum and increasing the mechanical properties.

3.2. Utilization of lignin as a binder

Sarkar and Adhikari (2012) investigated the adhesive strength and thermal stability of lignin-modified PR which were prepared by replacing phenol with lignin at different weight percentages. The thermal stability of lignin-modified PR was studied by DSC, TGA, and through isothermal analysis, and it was found that lignin-modified PR is more thermally stable than pure PR. The adhesive strength of 50% lignin-modified PR was determined through the lap-shear method, which showed that the lignin-modified resin retains 78% of the adhesive strength.

Tejado et al. (2006) investigated lignin as a promising natural alternative to petrochemicals in the production of PR, which are usually used as a binder, due to their structural similarity. Physico-chemical characterization of three types of lignin, namely kraft pine lignin, soda-anthraquinone flax lignin, and ethanol-water wild tamarind lignin was evaluated to determine which was the most suitable chemical structure for the above purpose. Both the structural and thermal characteristics suggested that kraft pine lignin would be a better PR substitute in a binder, as it presents higher amounts of activated free ring positions, higher molecular weight and higher thermal decomposition temperature.

Furthermore, Silveira et al. (2013) studied the behavior of brake pads produced through replacing PR by lignosulfonate up to a 40% weight ratio. In this study, ammonium lignosulfonate acted as a binder and was composed with PR, barite, graphite, alumina and aramid fiber. To test the modified brake pads, friction coefficient, mass wear and SEM analysis were employed. The results showed an average friction coefficient of approximately 0.4 and a

heterogeneous surface morphology. The satisfactory results were compatible with the current friction materials.

In addition, lignin-modified phenol formaldehyde resin (LPE) was studied for application to environment-friendly brake friction material. Lignin-modified phenol formaldehyde resin is prepared from methanol-soluble lignin through polymer blend methods. The chemical structure of LPE is characterized by ^{13}C NMR, and TMA and DSC analyses are conducted to evaluate the thermal behaviors. Flexural tests and brake dynamometer tests of samples prepared from LPF by compression molding are carried out, and the results are compared with those obtained for the samples prepared from commercial phenol formaldehyde resin (PF). Results of the flexural test showed that the LPE exhibits flexural strength equivalent to that of PF. Results of the brake dynamometer test showed that replacement of PF with LPE increased the fade resistance of the brake friction material at elevated temperatures (Kuroe et al., 2013).

3.3. Utilization of lignin as filler

The stabilizing effect of natural filler, sulfur-free lignin, on the thermal degradation of natural rubber was examined by Kosikova et al. (2006). Lignin was incorporated into natural rubber in amounts of 10~30%. It was shown that the lignin preparation used improved the physic-mechanical properties of the rubber vulcanizates. Thermogravimetric analysis and differential scanning calorimetry were used to study the thermal degradation of unfilled and lignin-filled vulcanized natural rubber. Measurements were carried out under atmospheric condition. It was revealed that lignin used as filler increased the resistance of natural rubber vulcanizates to thermal degradation in air.

Rozman et al. (1998) studied the effect of lignin as filler on the physical properties of coconut fiber-polypropylene composites. The study demonstrates that composites with lignin as filler possess higher flexural properties compared to the control composites.

In another study, lignin-based rubber vulcanizates were analyzed for physic-mechanical properties, oil and fuel resistance, and thermal stability, and compared with conventional fillers like PR and carbon black. Modified lignin has been found to produce elongation, hardness and compression set properties that were superior compared to PR, but inferior to carbon black. Resistance to swelling, however, depends on the type of oil or fuel, and modified lignin always showed better properties than carbon black. Both thermo-gravimetric analysis and thermo-mechanical analysis showed highest thermal stability for the modified lignin, followed by PR and carbon black (Setua et al., 2004)

4. Materials and Methods

4.1. Raw materials

Brake pad materials used in this study were based on a non-asbestos organic type formulation containing of 6 ingredients. The main materials were binder (phenol formaldehyde resins and lignin), fiber (EFB-empty fruit bunch), lubricant (graphite), abrasive (alumina) and filler (cashew nut shell liquid and lignin). As alternative materials, soda lignin (SL), sulfuric acid lignin (SAL) and heat-treated SAL (HL) were partially replaced with PR and CNSL. Soda lignin (Protobind 1000) was purchased from Granit Research and Development SA that had been generated through a soda process from herbaceous crops involving wheat straw and sarkanda grass. The sulfuric acid lignin was prepared by treating biomass with 72 wt% sulfuric acid (TAPPI method -T222 om-88). This residual lignin was usually generated in the pretreatment and acid hydrolysis steps from biochemical conversion of lignocellulosic biomass to bioethanol. The heat-treated sulfuric acid lignin was produced from sulfuric acid lignin. Briefly, sulfuric acid lignin was heat treated in the oven at a temperature in the range of 200°C and for an effective treatment time of 1hour.

The modified brake pad contained different ingredients of binder and filler as well as different amounts of each ingredient. In part 1, lignin was used as binder instead of PR up to 40%. In part 2, lignin was used as filler instead of CNSL up to 40%. The amounts of each of these ingredients in the composite material are shown in Tables 1 and 2, respectively.

Table 1. The amounts of raw material ingredients in the part 1 specimens

Raw material	Performance	Sample (wt%)				
		L-0%	L-10%	L-20%	L-30%	L-40%
Lignin	Binder	0	2.5	5	7.5	10
PR	Binder	25	22.5	20	17.5	15
EFB	Fiber	10	10	10	10	10
Graphite	Lubricant	7.5	7.5	7.5	7.5	7.5
Alumina	Abrasive	7.5	7.5	7.5	7.5	7.5
Barium sulfate	Filler	50	50	50	50	50

Table 2. The amounts of raw material ingredients in the part 2 specimens

Raw material	Performance	Sample (wt%)				
		L-0%	L-10%	L-20%	L-30%	L-40%
Lignin	Filler	0	5	10	15	20
CNSL	Filler	50	45	40	35	30
PR	Binder	25	25	25	25	25
EFB	Fiber	10	10	10	10	10
Graphite	Lubricant	7.5	7.5	7.5	7.5	7.5
Alumina	Abrasive	7.5	7.5	7.5	7.5	7.5

4.2. Structural and chemical analysis of lignin

To compare the chemical properties and structural features of three different types of lignin; Soda lignin, Sulfuric acid lignin and Heat-treated sulfuric acid lignin, they were characterized through several analytical procedures:

(1) Elemental analysis- weight percentage of carbon, hydrogen, oxygen, nitrogen and sulfur, (2) methoxyl group (OMe) and hydroxyl phenol group (Phe-OH)- main functional groups of lignin, (3) gel permeation chromatography (GPC)- average molecular weight (M_w), (4) Derivatization followed by reductive cleavage (DFRC)- frequency of the $\beta\text{-O-4}$ linkage and quantity of both G and S units.

4.2.1. Elemental analysis

Elemental analysis was performed to determine the carbon, hydrogen, oxygen, nitrogen and sulfur content in lignin samples using US/CHNS-932 (LECO Corp., USA). The oxygen content was calculated as a difference.

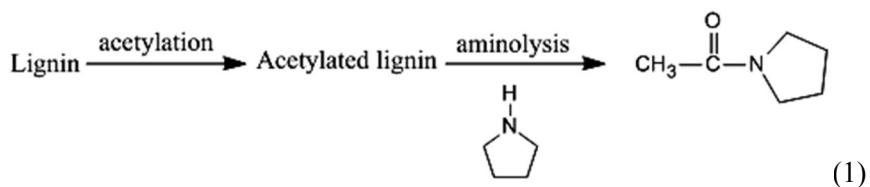
4.2.2. Methoxyl groups

Methoxyl group was determined through the method suggested by Vazquez et al (1997). The lignin (30 mg) was treated with 4 mL of hydriodic acid and heated for 30 min at 130°C in a heating block. After the sample was cooled on ice, an appropriate amount of internal standard (ethyl iodide) and 3 mL of pentane were added. The pentane phase was collected for GC analysis

of methyl iodide, released from lignin methoxyl groups, and ethyl iodide, internal standard.

4.2.3. Hydroxyl phenolic groups

To determine free phenolic hydroxyl groups in lignin, the acetylated lignin (20 mg), treated with pyridine and acetic anhydride (1:1, v/v), added to 0.5 mL of dioxane containing 20 μ l of 1-methylnaphtalene, was treated with 0.5 ml of dioxane-pyrrolidine (1:1, v/v) solution, which initiated the aminolysis reaction (1). After the addition of pyrrolidine, samples were taken from the reaction mixture at different times and analyzed through gas chromatography.



4.2.4. Gel Permeation Chromatography (GPC)

Molecular weights of lignin were determined by a GPC max instrument (ViscotekRlmax, Viscotek, UK) equipped with a PLgel3- μ m MIXED-D columns (300 \times 7.5 mm, VARIAN, Inc.), a PLgel 3- μ m MIXED-E column (300 \times 7.5 mm, VARIAN, Inc.), and a PLgel 5- μ m guard column (50 \times 7.5 mm, VARIAN, Inc.) using UV-Vis detection (VE3210, Viscotek) after acetylation of the lignins with pyridine and acetic anhydride (1:1, v/v) at 75°C for 6 h. Acetylated lignins (20 mg) were dissolved in tetrahydrofuran (THF) and analyzed using the GPC system. Calibration curves were created with

different molecular weights ranging between 580 Da and 3250,000 Da of polystyrenes.

4.2.5. Derivatization followed by reductive cleavage (DFRC method)

To determine the frequency of arylglycerol- β -aryl ether linkages (β -O-4), SL, SAL and HL were subjected to the DFRC method (Lu and Ralph, 1997). Essential DFRC products, acetylated coniferyl and sinapyl alcohol, were quantitatively determined through GC analysis (Agilent 7890A) on an instrument equipped with a capillary column DB-5 (30 m X 0.32 mm X 0.25 μ m, Agilent).

4.3. Thermal properties and chemical analysis of lignin

To compare the thermal decomposition behavior and chemical composition of three different types of lignin - Soda lignin, Sulfuric acid lignin and Heat-treated sulfuric acid lignin - they were characterized by several analytical procedures:

- (1) Chemical composition- lignin content and monomeric sugar composition,
- (2) Thermogravimetric analysis (TGA)- thermal decomposition characteristics.

4.3.1. Chemical composition of lignin

Acid insoluble/soluble lignin contents in Soda lignin, Sulfuric acid lignin and Heat-treated sulfuric acid lignin were determined by a Laboratory Analytical Procedure (LAP) from the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2004). Specifically, these lignins (ca. 0.3 g) were thoroughly mixed in 72% sulfuric acid (2 ml) at 30°C for 2 h. The hydrolysate was then diluted to 4% acid and cooked for 1 h at 120°C. The solution was vacuum filtered through a filtering crucible. The solid residues (acid insoluble lignin) were dried at 105°C overnight before measuring their weights. The monomeric sugars (acid soluble lignin) released from sulfuric acid hydrolysis of the solid residues were analyzed using high-performance anion exchange chromatography (HPAEC, Dionex) with a CarboPac PA10 column (4 x 250 mm, Dionex) using an ED50 pulsed amperometric detector (PAD). The resulting weight was corrected for the water content in order to obtain the water-free dry weight.

4.3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of lignins will be carried out using Q-5000 IR instrument (TA instruments, USA). TGA (weight loss as a function of temperature) and derivative thermogravimetry (DTG) analysis will be performed at a constant heating rate of 10 °C/min up to 800 °C in 25 ml/min flow of nitrogen atmosphere.

4.4. Procedure of manufacturing brake pad

Each type of lignin was mixed with other main raw materials using an agitator for 10 minutes at 125 rpm. All ingredients were in powder form. After the mixing process, the blended powder was put in the 30 mm- width 50 mm-length 20 mm- height stainless steel mold. Then, the samples were hot-pressed for 20 minutes using a hot pressing machine with 25 kgf/cm^2 pressure and 150°C temperature (Figure 4). The samples were then baked for 6 h in a 500°C post-curing process using a furnace to completely cure the PR.

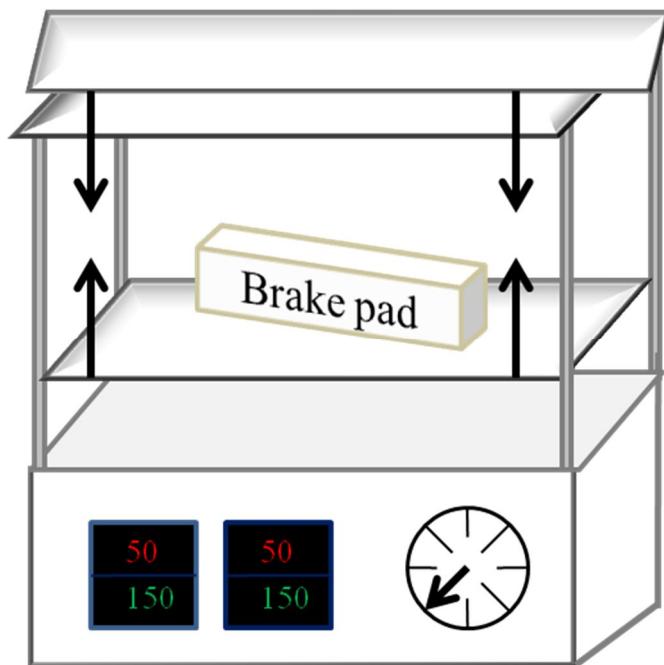


Figure 4. Diagram of hot pressing machine

4.5. Performance characteristics of modified brake pad

The braking performances and physical properties of brake pads based on SL, SAL and HL were evaluated based on several metrics: (1) friction coefficient- the resistance an object encounters in moving over another, (2) Mass wear- loss of material from a surface by means of some mechanical action, (3) Izod impact strength test- impact resistance properties, (4) Thickness swelling in water- effect of the absorbed water on its dimensions.

4.5.1. Friction coefficient and wear resistance

Figure 5 shows the equipment used to determine the frictional and wear behavior. Tests were conducted at Daegu Mechatronics & Materials Institute, Korea. All the tests were done with a pin on disc machine by sliding it over a cast iron surface at a load of 5 Kgf against a rotating brake drum, a sliding speed of 100 rpm and a processing time of 60 s. The friction coefficient was calculated from the friction force measured during the wear test, and the wear rates were calculated from weight loss measurements. Both tests were performed in ambient air with a temperature of $150 \pm 0^{\circ}\text{C}$.

4.5.2. Izod impact strength test

Izod impact testing is an ASTM D256 standard method of determining the impact resistance of materials. The test samples were trimmed to 60 x 10 x 10 mm with V-shape notch (2 mm). These samples were clamped into the impact machine with the notched side faced to the striking edge of the pendulum in the vertical position. The impact energy was expressed in Joule/m (J/m).

4.5.3. Thickness swelling in water and oil

The water and oil absorption behavior of the lignin based experimental brake pad and the effect of the absorbed water and oil on its dimensions were determined by soaking the samples in water for 24 h. Before the test, the weights of samples were measured. Subsequently, dimensions (thickness) of the samples were measured using a Vernier caliper. Next, after 24 h of submersion in water, all of the samples were oven-dried to obtain the increase in weights and dimensions.

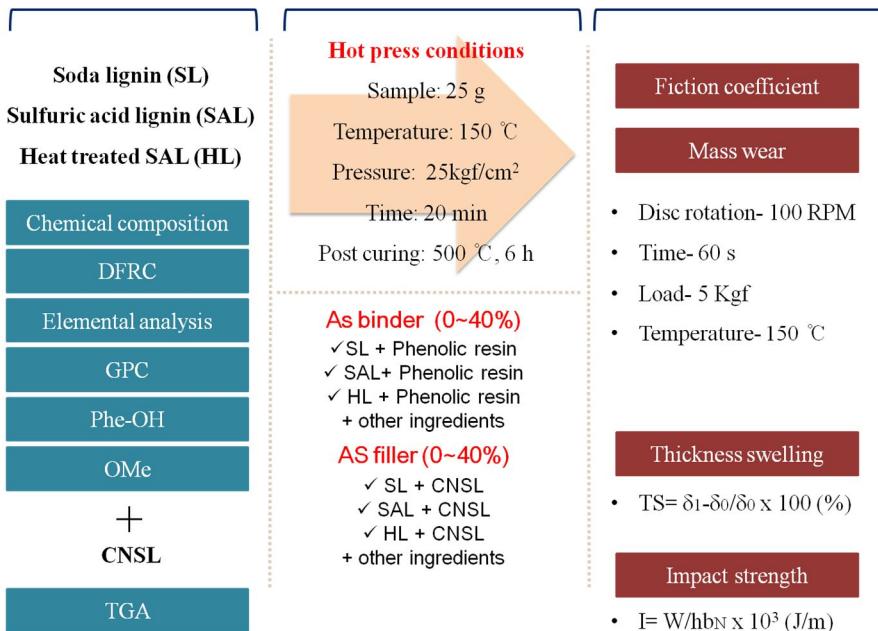
In the water immersion tests, thickness of each sample was measured to determine the thickness swelling (TS) by using the following equation:

$$\text{Thickness swelling (\%)} = \frac{(\delta_1 - \delta_0)}{\delta_0} \times 100 \quad (2)$$



**Figure 5. Equipment used to determine the friction properties
in this study**

4.6. Overall process



5. Results and Discussion

5.1. Lignin as binder

5.1.1. Structural and chemical analysis of lignin

5.1.1.1. Elemental analysis

Lignins vary in structure according to their method of isolation and their plant sources. In this study, three different sources of lignin (SL, SAL and HL) were adopted and applied for partial incorporation into phenol formaldehyde resin (PR) as binder and cashew nut shell liquid (CNSL) as filler, respectively. To investigate and reveal the chemical mechanism occurring between each lignins and PR, it is essential to analyze the lignin structure so the bonding reaction caused either chemically or physically between lignin and PR can be predicted. The structure and characteristics of lignin also significantly affect the performance value of the final product (modified brake pads).

Table 3 shows the results of the elemental composition obtained for the various technical lignins.

The elemental analysis of the technical lignins showed that SL had higher carbon content than the other lignins. For example, the carbon content of SL was 61.3%, compared to 50.1% for SAL and 60.1% for HL. Although the disparity in carbon content was insignificant, this presence of carbon enhances each friction layer of the samples; therefore, these higher carbon contents indicate an enhanced friction coefficient (Qi et al., 2014).

When the sulfur contained in each lignin is burned in air, it reacts with the oxygen in the air to form sulfur dioxide (SO_2), which produces an irritating, rotten smell. This feature may cause odor both during the brake pad production and braking system working. However, according to the findings for sulfur content shown in Table 3, SL has only 1.1% sulfur content and 0.5% for SAL, 0.6% for HL, respectively, which indicates that the possibility of odor will also be negligible. On the other hand, formaldehyde, which is contained in PR, causes an overpowering stench, which is incomparably stronger than the SO_2 occurring from lignin. Formaldehyde is classified as a volatile organic compound (VOC). VOCs are chemicals that become a gas at room temperature. As a result, products made with formaldehyde will release the gas into the air. This is called off-gassing. If high concentrations of formaldehyde are off-gassed, it causes a strong pickle-like odor. Actually, during the experiment, the odor became severe when the PR content was gradually increased.

The ring hydrogen in the *para*- and both *ortho*- positions relative to the hydroxyl group can react with formaldehyde and thus cross-link to form a three-dimensional network which leads to improved adhesion (Ibrahim et al., 2011). The results indicated that SL had higher hydrogen content (7.3%) than SAL (5.2%) or HL (4.5%), and thus it can be expected that the frequency of the cross-link between PR and SL will be improved compared to other lignins (SAL and HL).

Table 3. Elemental composition of SL, SAL and HL

Sample	Elemental composition					(%)
	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	
SL	61.3 (1.0)	7.3 (0.2)	29.6 (1.2)	0.7 (0.0)	1.1 (0.0)	
SAL	50.1 (1.3)	5.2 (0.2)	34.3 (1.5)	0.5 (0.0)	0.5 (0.2)	
HL	60.1 (0.6)	4.5 (0.1)	34.3 (1.2)	0.5 (0.1)	0.6 (0.1)	

5.1.1.2. Functional groups and molecular weight

The final adhesive property of the lignin is significantly dependent on the structural and chemical features of the lignin, including the functional groups (OMe and Phe-OH) and molecular weight. As such, a complete characterization of the technical lignin is extremely necessary prior to the incorporation of lignin into PR as a binder (Yang et al., 2014).

As shown in Table 4, SL also had higher OMe contents (16.7%) and a larger concentration of Phe-OH groups (3.0%) than SAL (0.9%, 14.1%) or HL (0.3%, 13.3%). This higher OMe content indicated that the SL had more open *meta*- positions on its phenyl ring and was therefore suitable for increased chemical bonding between lignin and PR. Furthermore, the number of Phe-OH groups essentially affected the reactivity of the lignin (Sarkar and Adhikari, 2000). Therefore, the presence of this group tended to increase the reactivity of lignin toward PR. SL had the highest proportion of Phe-OH groups due to the method used in the pulping process, which caused the extensive degradation of the ether bonds of lignin due to the use of sodium hydroxide (Abda-Alla et al., 1998). The results of both functional group contents have similar tendency with the results of hydrogen contents in lignin shown above.

As shown in Table 4, HL had an increased Mw of 3,330 Da compared to that of the SAL (2,266 Da), which reflected the condensation from heat treatment. This condensation acted as an obstacle to friction performance when used as binder. In addition, HL had a high PDI of 3.0%, which indicates a high fraction of high-molecular weight molecules. This lignin with a high fraction of high-molecular weight molecules was less likely to polymerize with PR and had weaker adhesive properties.

Table 4. Functional groups, and the average molecular weight and polydiversity index of SL, SAL and HL

Sample	Molecular weight		Functional groups (%)	
	Mw (Da)	PDI (Mw/Mn)	Phe-OH	OMe
SL	3698	2.4	3.0 (0.2)	16.7 (0.0)
SAL	2266	1.4	0.9 (0.0)	14.1 (0.5)
HL	3330	3.0	0.3 (0.3)	13.3 (0.2)

5.1.1.3. Derivatization followed by reductive cleavage

The levels of uncondensed arylglycerol- β -aryl (β -O-4) ether linkages in the lignin were determined through DFRC (Table 5). Since DFRC analysis selectively cleaves the β -O-4 linkage and releases acetylated C6C3 type monomers [acetylated coniferyl (G unit) and sinapyl alcohol (S type)] as DFRC products, the frequency of the β -O-4 linkage and quantity of both G and S units in the lignin can be indirectly evaluated through the quantification of the DFRC products.

Table 5 lists the quantitative amounts of DFRC products from SL and SAL. Due to limited solubility no data was obtained for HL. Low ether linkage levels (G+S) were obtained for both lignin samples (<100 $\mu\text{mol/g}$), as expected, since these were highly processed lignin. SL showed higher G content (77.2 $\mu\text{mol/g}$) than that of SAL (60.7 $\mu\text{mol/g}$). For the S content, SL had 76.4 $\mu\text{mol/g}$ and it was not detected in the SAL sample.

The presence of G unit in both lignins (SL and SAL) confirmed that both lignins had potential active sites for polymerization. In phenol formaldehyde condensation reactions, phenol condenses initially with formaldehyde in the presence of alkaline to form methylophenol (Pizzi et al., 1983). The initial attack may be at the 2-, 4- or 6- position, as shown in Figure 6. The second stage of the reaction involved the reaction of methylol groups with other available phenols or methylophenols, leading first to the formation of linear polymers and then to the formation of hard cure and highly branched structure.

The similarity between G unit of lignin and phenol (Figure 6) revealed that lignin could also react with formaldehyde and could be cross linked with formaldehyde in the same way as in the phenol formaldehyde condensation reaction, as shown in Figure 7. Thus, the free 3-position of G units in both

lignins gave significant values compared to S-type unit, which had both the 3-position and 5-position attached to the methoxyl group, preventing the occurrence of a polymerization reaction.

Table 5. Quantitative analysis of DFRC products of lignin

Sample	Amount (umol/g sample)			
	G- CH=CHCH ₂ OAc (Acetylated CA)	S- CH=CHCH ₂ OAc (Acetylated SA)	Total	S/G ^a
SL	77.2 (3.7)	76.4 (8.2)	153.6 (11.9)	0.3 (0.1)
SAL	60.7 (2.3)	-	60.7 (2.3)	0.0 (0.0)
HL	-	-	-	-

^a Average molar ratios of sinapyl alcohol/coniferyl alcohol formed by the cleavage of β-O-4 linkages.

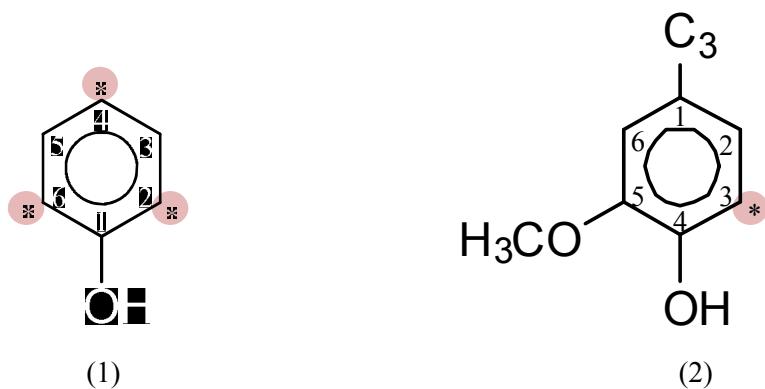


Figure 6. (1) Phenol structure with three reactive sites: 2-, 4- and 6-position and (2) lignin structure with 1 reactive site: 3-position

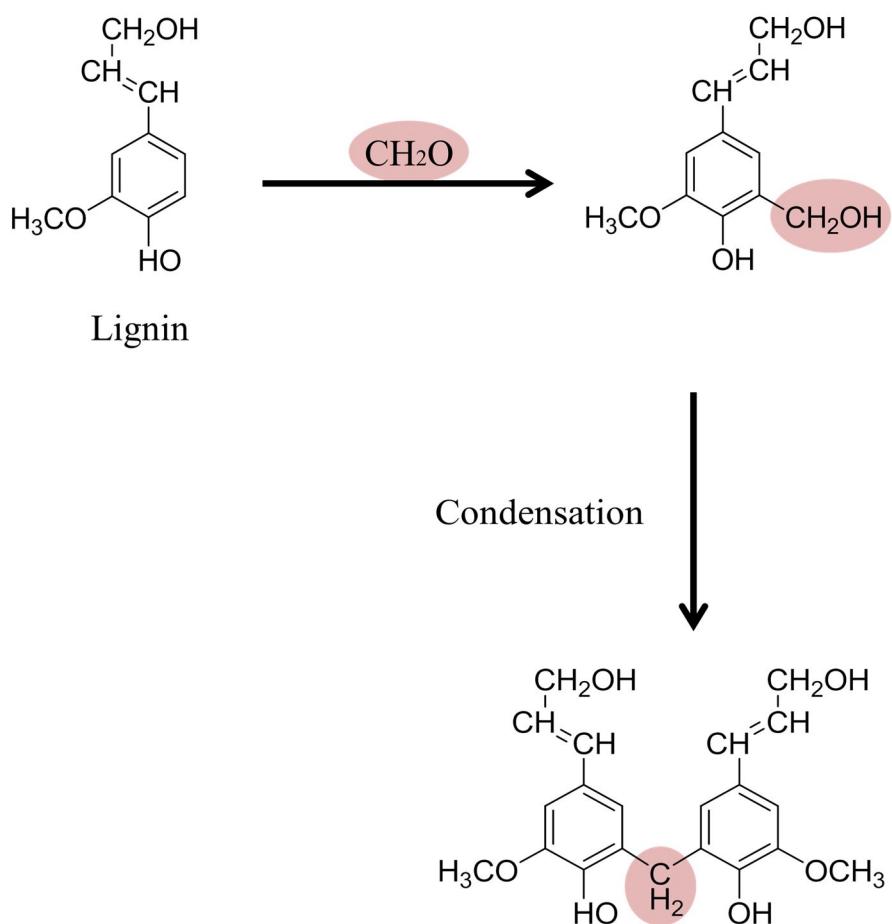


Figure 7. Cross-linking between lignin and formaldehyde

5.1.2. Performance characteristics of the modified brake pads

5.1.2.1. Friction coefficient and wear resistance

Figure 8 and Figure 9 show the findings related to friction coefficient and wear resistance of the modified brake pads with lignin as a binder, respectively.

The SL-based brake pads exhibited a significant improvement in every area, and the friction coefficient of the SL-40% sample reached 0.6, while the SAL- and HL-based brake pads showed decreasing trends as the lignin content increased. These results corroborate the results of the functional group analysis shown above. The observations obtained from the performance test supported the theory that the friction was enhanced with a larger number of activated sites in lignin. SL was a better raw material for a binder because it had more active sites than the other lignins (Pizzi et al., 1989). These numerous active sites allow better interfacial bonding - namely, polymerization - with PR. The polymerization reaction with PR contributed not only to the friction coefficient, but also to the impact strength and thickness swelling in water.

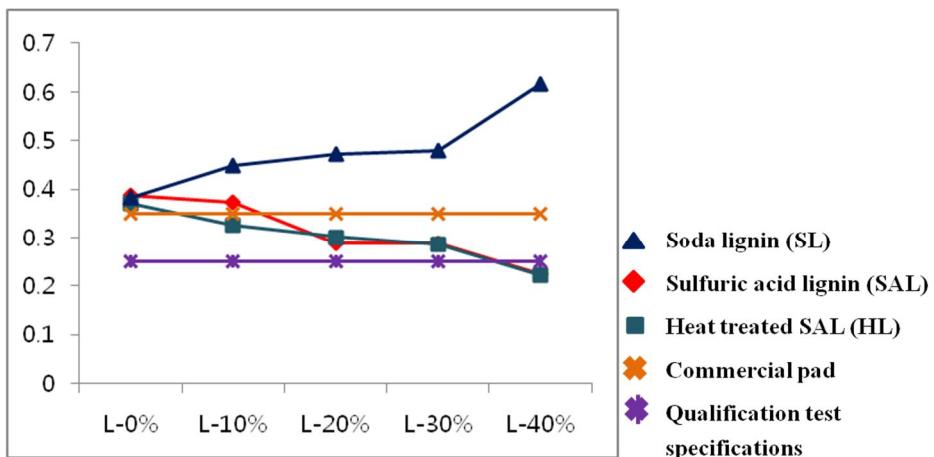


Figure 8. Change in the friction coefficient at 150 °C when lignin was used as a binder in brake pads

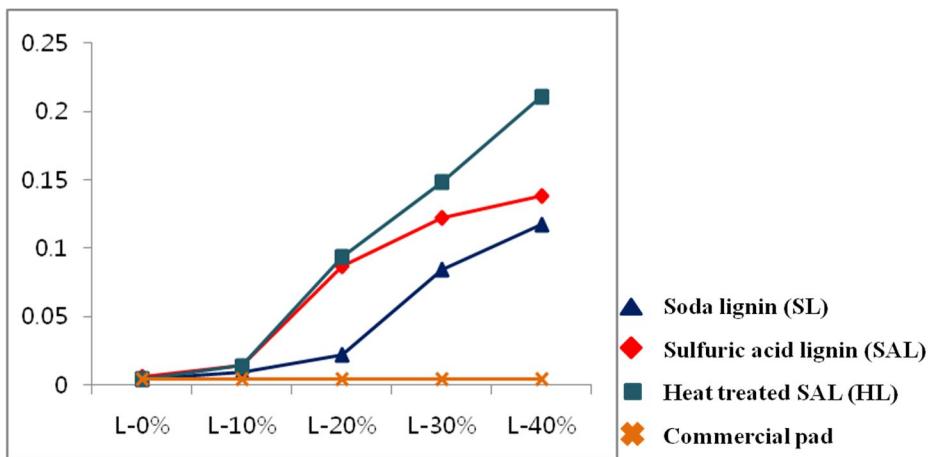


Figure 9. Change in the specific wear rate when lignin was used as a binder in brake pads

5.1.2.2. Impact strength and thickness swelling in water

The changes of the impact strength and thickness swelling in water test including commercial brake pads value are shown in Figure 10 (impact strength) and Figure 11 (thickness swelling in water).

The SL-based brake pad had the highest impact strength of 27.2 J/m (L-10%) and a smaller thickness swelling in water of 0.6% (L-40%). The gradual increase in impact strength or decrease in thickness swelling were attributed to the decreased number of pores due to the close interface packing achieved between PR and lignin. Meanwhile, the amount of dust generated during the wear resistance test increased to 0.21 g for the HL-based brake pads, 0.14 g for SAL, and 0.12 g for SL when the lignin content was increased; these are large amounts compared to that of the commercial brake pads (0.004 g). This result is due to the decreased wear resistance resulting from the presence of lignin. According to Qi., char formed by the degradation of organic ingredients had a positive effect on wear rate. Therefore, the problem mentioned above can be improved by adding carbonized char produced from lignin degradation (Qi et al., 2014).

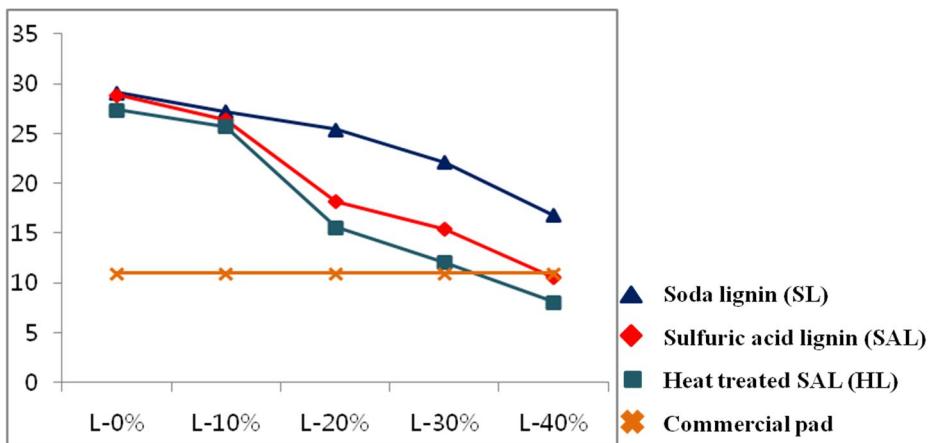


Figure 10. Impact strength values of brake pad composed with lignin as binder

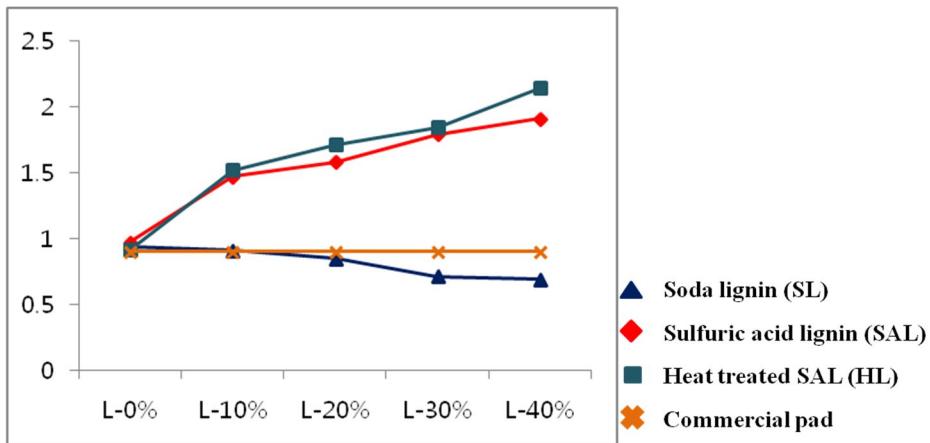


Figure 11. Variation of thickness swelling in water of brake pad composed with different lignins and percentages of ingredients as a binder

5.2. Lignin as Filler

5.2.1. Thermal property and chemical analysis of lignin

It was essential to investigate the thermal properties and chemical composition of each type of lignin, as these characteristics significantly affect the performance characteristics of the final product.

Table 6 shows the results of lignin and monomeric sugar content in SL and SAL, together with corresponding Mw and PDI for SL, SAL and HL. In this table, the term “lignin content” represents Klason lignin, which is the residue that remains after solubilizing the carbohydrate with a strong mineral acid. As shown in the results, SL contains 93.4 wt% of acid insoluble lignin and 4.1 wt% of acid soluble lignin, while SAL contains 51.3 wt% of total lignin, which is only half the amount in SL. This result indicates that SAL has other contaminants besides lignin, such as monomeric sugars (arabinose, galactose, glucose, xylose, mannose). For this reason, heat treatment proceeded for SAL to remove contaminants. As a final product, HL was obtained. By comparing SAL and HL, the effects of different lignin contents on the performance of brake pads can be assessed.

Table 6 also shows that HL had a higher Mw than SAL, which reflects condensation due to heat treatment. This condensation plays a key role in the friction performance of each filler. In addition, HL has a high PDI, which indicates that HL has a high fraction of high molecular weight. This high Mw lignin is suitable for combination with CNSL, as it will strengthen, reinforce and maintain the structure of the brake pad.

The registered TGA curves of technical lignins and CNSL are compared in Figure 12 and Figure 13. In general, when braking an automobile, the

temperature applied to the brake pad rises up to 300-400°C. At this time, fillers act as a resistor to the heat. Therefore, to be used as filler, a material's thermal stability is extremely important. According to the TGA data, CNSL, which is widely used as commercial ingredient for filler, starts to decompose at approximately 427°C. Similarly, as seen in the data collected, the three lignin decompositions also proceeded in the range of 300-400°C. However, when comparing TG curves, while CNSL is degraded rapidly at 400°C, lignins begin to decompose at approximately 200°C, and decomposition proceeds very slowly, terminating at nearly 800°C, which indicates the possibility of greater thermal stability of lignins as fillers. Weight loss at a temperature of 200°C, shown in SAL, may be attributed to the decomposition of carbohydrate moiety (Qi et al., 2014). By removing these contaminants through heat treatment at 200°C as shown above, we could obtain HL, which has a relatively high thermal stability compared to other lignins.

Table 6. Chemical compositions and the average molecular weight with polydiversity index of lignins

Sample	Lignin (wt%)		Monomeric sugar (wt%)	Ash	Total	Mw (Da)	PDI (Mw/Mn)
	Acid insoluble lignin	Acid soluble lignin					
SL	93.4 (0.2)	4.1 (0.0)	1.5 (0.0)	1.7	100.7	3698	2.4
SAL	50.0 (0.4)	1.3 (0.1)	30.5 (3.5)	2.2	84.2	2266	1.4
HL	-	-	-	-	-	3330	3.0

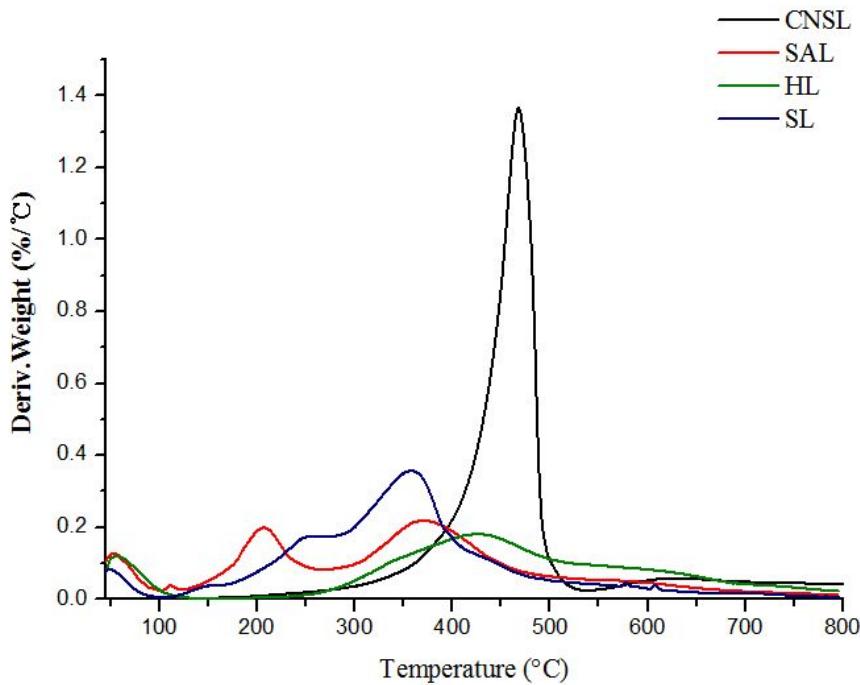


Figure 12. DTG curves for CNSL, SAL, SL and HL (10°C/min, up to 800°C, N2 flow)

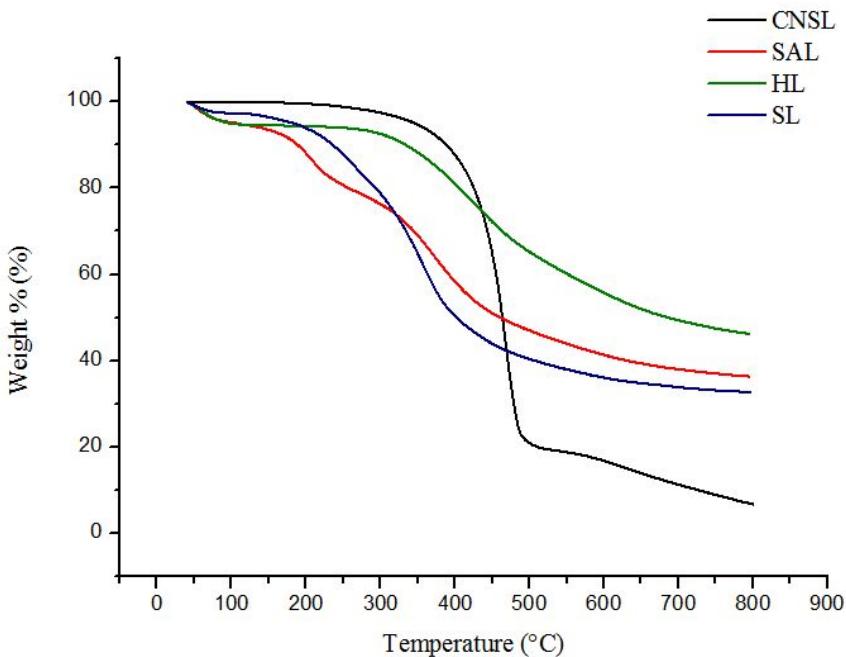


Figure 13. TG curves of CNSL, SAL, SL and HL (10°C/min, up to 800°C, N2 flow)

5.2.5. Performance characteristics of the modified brake pad

Figures 14, 15, 16, and 17 show the results of friction coefficient testing, wear resistance, impact strength and the thickness of swelling in water, respectively, for all modified brake pads with lignins as fillers.

When lignin was used as a filler, HL-based brake pads demonstrated better properties in every performance metric compared to other samples, as shown in Figures 14, 15, 16, and 17.

The performance of lignin-based brake pads was effectively improved compared to commercial pads, especially for the sample with 10% HL in friction coefficient, which was 0.5. As shown above in the TGA result, HL was much more stable at a high temperature (440°C) than the other lignins, which can be explained by the fact that HL probably has the most condensed structure, providing an improved friction coefficient and added strength to the brake pad. In addition, HL also has a higher possibility of char production than SL or SAL, which is one of the main products of the thermal decomposition of lignin. This char has been proven to have a positive effect on wear resistance in brake pads (Sutikno et al., 2010). Due to thermal degradation during the wear resistance test, the amount of carbon, presented in the form of char, increases in the friction layer of samples and contributes to stabilizing the structure of brake pads, and thus the dust emission that is generated during braking of the automotive is reduced (Qi et al., 2014).

Compared with SAL, HL-based brake pads have a higher impact strength and less thickness swelling in water, which varied from 20.5 J/m to 30.4 J/m and from 0.5% to 3.0% respectively, while SAL remained at 26.8 J/m in terms of impact strength and 0.6% swelling thickness. It can be assumed that these results are related to the carbohydrate moiety in SAL, which has a negative

effect on strength and moisture resistance. According to Jung et al., lignin is much less hydrophilic than carbohydrates, which prevents the absorption of water (Jung et al., 1993). The carbohydrate content in SAL results in reduced water resistance and impact strength. When SAL-based brake pads are exposed to water, large amounts of water are absorbed by the filler, causing the structure of the brake pad to become mushy and weakening the impact strength.

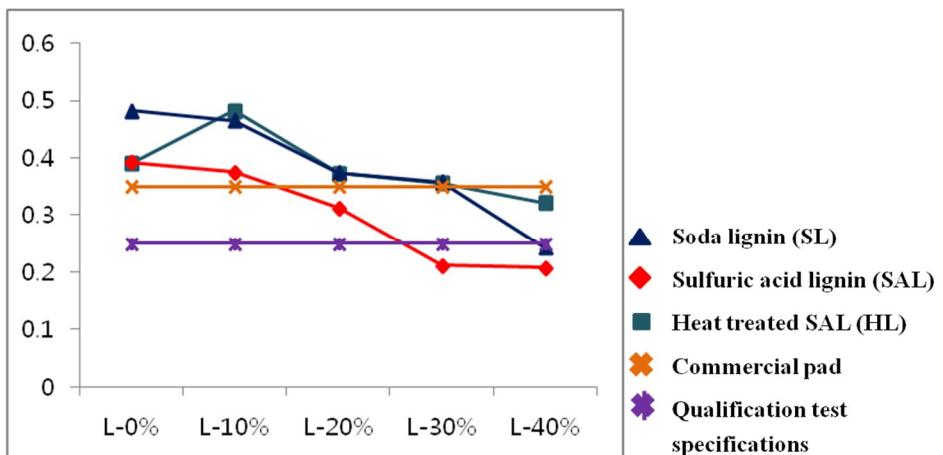


Figure 14. Change in the friction coefficient at 150 °C when lignin was used as a filler in brake pads

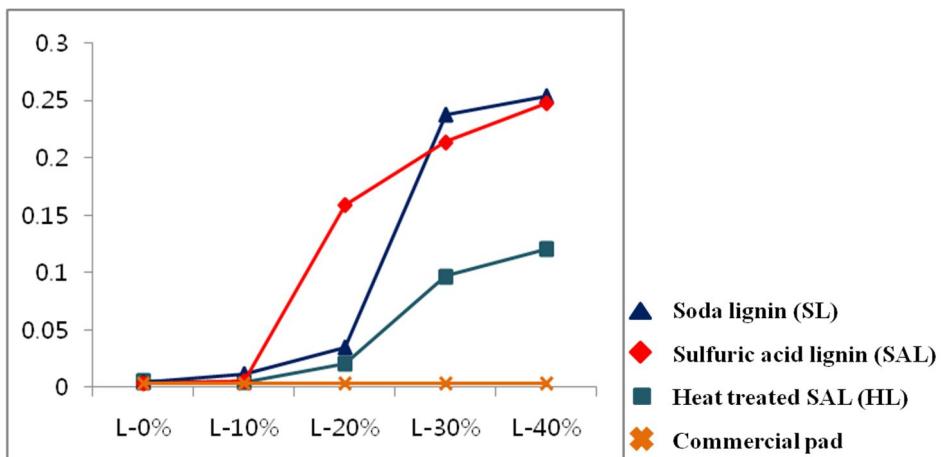


Figure 15. Change in the specific wear rate when lignin was used as a filler in brake pads

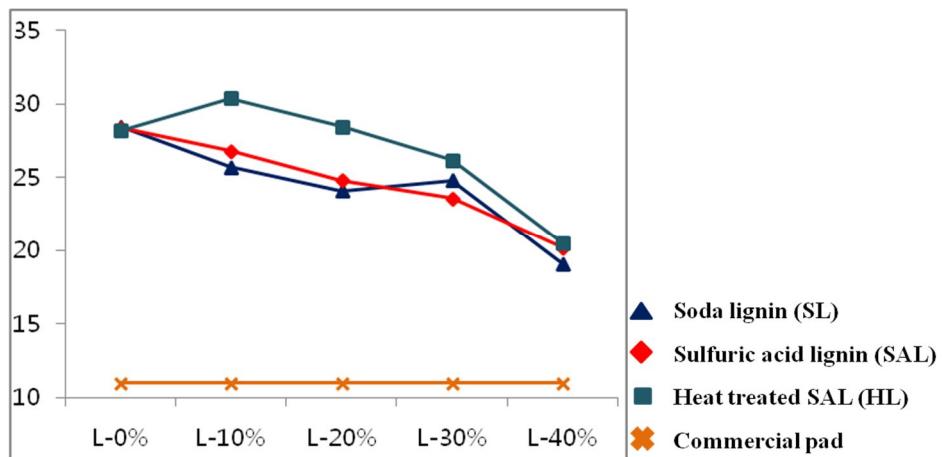


Figure 16. Impact strength values of brake pad composed with lignin as filler

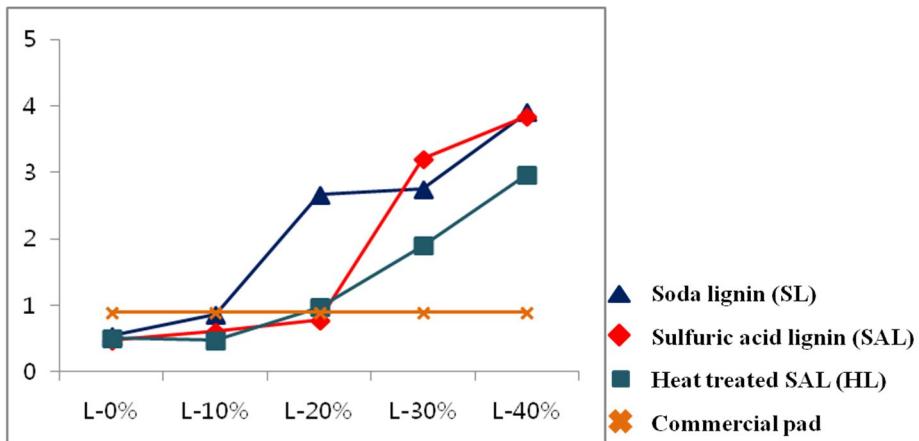


Figure 17. Variation of thickness swelling in water of brake pad composed with different lignins and percentage of ingredients as a filler

6. Conclusion

Eco-friendly brake pad materials were prepared and chemically characterized using several analytical methods in order to evaluate their suitability for incorporation into PR. Then, the performance of the modified brake pads was tested. When lignin was used as a binder in the brake pads, the SL added in the formulations was shown to have very advantageous effects in terms of stabilizing the friction coefficient and improving impact strength and thickness swelling in water.

In general, as the content of lignin increased, the performance of the brake pads decreased slightly, except for the results for the friction coefficient with SL as the binder. The utilization of natural components in brake pads represents an important direction in development, with the aim of designing and manufacturing eco-friendly brake pads.

When lignin was used as a filler in brake pads, HL demonstrated the best performance in every parameter tested. Through the confirmation of the analyses and characterization results of HL, it was concluded that char, generated from the thermal degradation of lignin during the braking test, played an advantageous role in the performance of HL, particularly in wear resistance. In general, as the lignin content increased, the performance of brake pads decreased slightly. However, brake pads containing 10% lignin were considered sufficiently suitable, as they showed better performance than that of commercial brake pads.

7. References

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초 록

바이오매스의 주요 구성성분인 셀룰로오스를 선택적으로 활용하는 바이오에탄올 제조 및 화학펄핑 공정에서는 바이오매스의 또 다른 구성성분인 리그닌이 부산물로 다량 발생하는데, 이러한 부산물은 화석자원을 대신하여 바이오매스 기반인 고부가가치 제품으로 전환될 수 있는 잠재력을 보유하고 있다.

최근 자동차 브레이크 패드에서 발생되는 결합제인 페놀포름알데히드수지의 환경문제와 충진제인 캐슈 너트 껍질액의 소재 비용 증가 문제를 해결하기 위한 연구가 활발히 진행됨에 따라 보다 경제적이고 안정적인 친환경 마찰 소재의 개발에 관심이 모아지고 있다.

본 연구에서는 화학펄핑 공정에서 유래한 Soda lignin (SL), 당화 잔사인 Sulfuric acid lignin (SAL) 과 열처리한 SAL (Heat treated SAL; HL) 부산물을 브레이크 패드의 결합제와 충진제로 각각 사용하여 브레이크 패드 제조 가능성을 평가하였다. 이들이 브레이크 패드 내에서 결합제 및 충진제로서 작용하는 메커니즘을 밝혀내기 위해 리그닌의 열/화학적/구조적 특성을 분석하였으며, 리그닌의 종류 및 페놀포름알데히드수지와 캐슈 너트 껍질액에 대한 리그닌 대체 함유량 변화(0 ~ 40%)에 따른 브레이크 패드의 동마찰계수, 내마모성, 충격 강도 그리고 두께 팽창률의 변화를 측정하였다.

각 리그닌의 대표 관능기(Phen-OH, OMe) 정량분석, 리그닌 내 존재하는 G, S unit 빈도수 측정 등의 구조분석 결과에 의하면 SL은 SAL, HL에 비해 폐놀성 하이드록실기 함량이 최대 10배 높았으며, 이를 통해 SL이 다른 두 리그닌에 비해 포름알데히드와의 결합 가능성이 높은 구조를 지니고 있음을 확인할 수 있었다. 또한, HL의 열중량 분석 결과 SL과 SAL에 비해 고온에서 질량 손실 변화가 상당히 낮게 나타났으며, 이는 탄소를 함유한 탄 생성 비율이 더 높을 뿐만 아니라 상대적으로 높은 축합도에 기인하는 것으로 판단된다.

리그닌을 결합제로 이용한 브레이크 패드 성능 시험 결과에서는 모든 시편의 경우, 리그닌 함량이 증가함에 따라 동마찰계수가 감소하였지만, SAL-40%(0.2)를 제외한 대부분의 시편은 SAE (society of automotive engineers)에서 제시하는 상용 브레이크 패드의 동마찰계수 규격(0.3)보다는 높은 값(0.3~0.6)을 나타내었다. 특히 SL을 함유한 브레이크 패드는 동마찰계수뿐만 아니라 내마모성(0.009 g), 충격강도(16.8 J/m) 그리고 두께 팽창률(0.6%) 등 모든 시험 결과에서 다른 두 리그닌에 비해 향상된 성능을 나타내었다. 이러한 결과는 다른 두 리그닌에 비해 SL 내 존재하는 높은 폐놀성 수산기(3%)와 탄소 함량(61.3%) 등의 결과로부터 기인한 것으로 사료된다.

반면, 리그닌을 충진제로 사용한 브레이크 패드의 경우에는 HL에 기반한 브레이크 패드가 SL과 SAL에 비해 전체 시험범위에서 훨씬 우수한 성능을 나타냈다. 특히, 내마모성 분석 결과에 의하면 리그닌 함량이 높아질수록 내마모성은 저하되는 경향을 보였지만,

SL 또는 SAL 기반 브레이크 패드와 비교하여 HL 을 기반으로 한 브레이크 패드의 마모 분진 발생량은 최대 52%까지 감소하였다. 이러한 결과는 각 리그닌의 분자량 분석 그리고 열중량 분석을 통해 확인할 수 있듯이 HL 의 높은 열 안정성과 고도로 축합된 구조에 의한 것으로 판단된다.

결론적으로 리그닌을 첨가한 브레이크 패드는 동마찰계수, 내마모성 그리고 두께 팽창률 시험 등에서 상용 브레이크 패드 성능 수준에는 미치지 못하였지만 SL-40%를 결합제로 첨가한 브레이크 패드는 동마찰계수가 0.6으로 상용 브레이크 패드의 동마찰계수(0.3)보다 우수한 성능을 나타내었으며, HL 충진제를 기반으로 한 브레이크 패드는 내마모성, 충격강도 그리고 두께 팽창률 시험에서 각각 0.021 g, 30.4 J/m 그리고 1.9% 로 다른 두 리그닌에 비해 성능이 향상된 것을 확인할 수 있었다. 이상과 같이 본 연구는 리그닌 부산물의 친환경 브레이크 패드 결합제 및 충진제로서의 활용 가능성을 제시함으로써 농학 석사학위 논문으로서의 가치가 충분하다고 사료된다.