Development of Refined Natural Resin based Cashew Nut Shell Oil Liquid (CNSL) for Brake Pads Composite

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Abstract. Brake is one of the most important components in the vehicle. One type of brake that widely used is brake-based composites. One of the manufacture of composite material is resin. Cashew Nut Shell Liquid (CNSL) is a natural material which has chemical structure similar to synthetic phenol so it can be an alternative as a resin. Brake pads manufacture using CNSL as resin composites made to obtain the brake which is strong, wear-resistant, and environmentally friendly. The composite made using powder metallurgy techniques by mixing ingredients such as rubber, fibre glass, carbon, mineral sands and phenolic resin. Two formulas were composed by varying the resin and iron mineral sands in 5 grams. Composites were tested using Universal Testing Machine (UTM). The tensile strength result of those formulas are 600 N and 900 N and the elongations are 1.98 mm and 2.59 mm respectively. Formula 2 has a better tensile strength due to the addition of more resin is 15%. Since the better properties, formula 2 was derivated to 4 extended formulas and showed excellent pressure strength reached 20.000 N. It indicates that the addition of the resin can improve the mechanical properties of a composite.

1. Introduction
Brake pads is either of motor vehicles component that serves to slowing down or stop the vehicle, especially for a ground vehicle. The purpose of friction brakes is to decelerate a vehicle by transforming the kinetic energy of the vehicle to heat, via friction, and dissipating that heat to the surroundings. As a part of a commercial truck or automobile, brake materials have additional requirements, like corrosion resistance, light weight, long life, low noise, stable friction, low wear rate, and acceptable cost versus performance. In order to achieve the properties required of brakes, most brake materials are not composed of single element or compound, but rather are composites of many materials. More than 2000 different materials and their variants are now used in commercial brake components [1].

Development of the composite-based brake pads will reduce the damage of train wheels and sparks during braking continually, one way to do engineering materials using nature-based phenolic resin. Cashew Nut Shell Liquid (CNSL) is an oil composed from a complex phenolic compounds with...
long carbon chain branched and unsaturated [2]. Utilization of CNSL and its derivatives product in various industries increasingly open, including pharmaceutical industry; insecticides; adhesives; varnishes and paints, brake pads and clutch plate vehicles, laminating resin, and epoxy resin [3]. The main components of CNSL composed by acidic compounds such as anacardic acid; cardanol; and cardol, which is a nature phenolic compound that has many advantages when it compared with synthetic from petroleum derivatives. CNSL is a renewable resource, where the availability of raw material can be guaranteed, different from synthetic phenolic of petroleum derivatives which the prices and existence depend on petroleum abundance. Indonesia had imported phenol in form phenol and phenol resin as much as 53,640 tonnes/year, so that the potential of CNSL in Cashew Nut skin can be explored properly, there will be foreign exchange savings due to a reduction in imports of phenol with their natural phenol substitution of CNSL. The CNSL compounds and their derivatives are environmental friendly products, so it chance to replace the phenolic resin as brake pads composite[4].

2. Experimental

2.1. Decarboxylation of CNSL

The extracted CNSL (100 g) was mixed with toluene (150 mL) in a round bottom flask and refluxed for 3 hours by using dean-stark apparatus and check the TLC for the absence of anacardic acid. Then the decarboxylated CNSL (50 g) and 200 mL methanol were placed in a 500 mL round bottom flask. Then 20 mL of 40% formaldehyde solution and 3.0 mL diethylenetriamine were added in this solution. This mixture was heated until boiling under reflux for 2 hours. After the solution was allowed to reach room temperature, a phase separation occurred, showing a slightly reddish upper solution, and a dark brown solidified lower phase. The upper phase was subsequently decanted, and treated with distilled water (40 mL) followed by petroleum ether. The petroleum ether layer was evaporated to dryness, yielding a reddish residue of cardanol (26 g).

2.2. Pellet preparation

Preparation of pellets were conducted by mixing all the ingredients named Formula 1 (F1) and Formula 2 (F2) shown in Table 1.

| Material | (F1) | Gram | (F2) | Gram |
|----------|------|------|------|------|
| Resin    | 13   | 0.65 | 15   | 0.75 |
| Elastomer| 10   | 0.50 | 10   | 0.50 |
| Fibre    | 13   | 0.65 | 13   | 0.65 |
| BaCO₃    | 14   | 0.70 | 13   | 0.65 |
| Al₂O₃    | 9    | 0.45 | 9    | 0.45 |
| CaCO₃    | 14   | 0.70 | 13   | 0.65 |
| MgCO₃    | 9    | 0.45 | 9    | 0.45 |
| TiO₂     | 9    | 0.45 | 9    | 0.45 |
| Carbon   | 9    | 0.45 | 9    | 0.45 |

After all the ingredients are mixed, and then pressed for 15 minutes at a temperature of 160 °C use hot press, the resulting pellet was heated at 150 °C for 30 minutes. Formula 2 was derivated to extended Formula 2 (Table 2.)
Table 2. Extended Formula 2 for brake pads composite preparation

| Formula          | Concentration |
|------------------|---------------|
| Resin (CNSL/Phenolic) | 0/0.75, 0.0375/0.712, 0.065/0.675, 0.097/0.6375, 0.13/0.6 |
| Fibre Glass      | 0.65, 0.65, 0.65, 0.65, 0.65 |
| BaCO$_3$         | 0.65, 0.65, 0.65, 0.65, 0.65 |
| Al$_2$O$_3$      | 0.45, 0.45, 0.45, 0.45, 0.45 |
| CaCO$_3$         | 0.65, 0.65, 0.65, 0.65, 0.65 |
| MgO              | 0.45, 0.45, 0.45, 0.45, 0.45 |
| TiO$_2$          | 0.45, 0.45, 0.45, 0.45, 0.45 |
| Carbon           | 0.45, 0.45, 0.45, 0.45, 0.45 |

2.3. Brake pad Composites Characterizations
The extracted cardanol was characterized by FTIR spectroscopy to determine the functional groups contained in the extract, especially hydroxyl groups that can be used to bind other compounds. While the Thermal properties of the cardanol were determined by simultaneous thermal analyzer. Tensile strength specimen was conducted by UTM M500 50CT to know how much resistance tensile strength of the specimen is and SEM was used to determine morphological appearance in micro scale.

3. Result and Discussion
Development the composite-based brake pads aim to reduce the damage of train wheels and sparks during braking continually. By the improvement of the compositions of brake pads as an engineering materials using nature-based phenolic resin, we hope the mechanical properties as well as chemical properties have been upgraded. Cashew Nut Shell Liquid (CNSL) is an oil composed from a complex phenolic compounds with long carbon chain branched and unsaturated [2].

CNSL extraction that's done using hot water, which is then dried to remove water from the extract of physical separation by centrifugation. Meanwhile, if we want a more pure fractions, it can be done by further distillation, or with the extraction treatment using an organic solvent. Based on the research results, the main structure CNSL is 90% anarcadic acid and 10% cardol, but in detail components in the CNSL separated will depend on the treatment path will be executed. The increase in the levels of cardanol done through extraction using semi-polar and non-polar solvent.

Raw CNSL has a high relative density because it has anarcardic acid as the major fraction, there is intermolecular attraction between the electronegative oxygen atom and the partially positive hydrogen atom of the phenol core as a result the molecules are closely packed together [5]. The structure of anacardic acid, cardol, cardanol and 2-methyl-cardol were founded in crude CNSL showed in Figure 1. CNSL compound was added as a resilience in the binder system and reduces brake noise.
FTIR analysis of technical CNSL and decarboxylated CNSL result were shown in Figure 2. Infrared spectra absorption were in the regions of 3424 cm$^{-1}$, 2700-2900 cm$^{-1}$, 1615 cm$^{-1}$, 1200-1600 cm$^{-1}$, and 500-700 cm$^{-1}$ representing as -OH hydroxyl, C-H stretching, C-O, C=C aromatic stretching, and aromatic ring respectively. The presence of –OH hydroxyl has a role as a reactive group which will react with other components of composite material, so that CNSL can be used as an alternative of phenolic resin. But, raw CNSL still content impurities so that needed decarboxilation procedure to remove the impurities. The difference of two FTIR spectras indicate the lose of C-O from minor anacardic acid. CNSL based resin possess an outstanding resistance to the sulfiding action of mineral oils and high resistance to acids and alkalis [6]. In addition, high thermal stability also become one of requirement to be resin.
Simulant Thermal Analysis (STA) for the determination of thermal resistance of materials. Based on thermal analysis using STA indicated that the CNSL has high stability in temperature under 400 °C, proved by the small decrease of its mass in the temperature range of 0 - 350 °C. Nevertheless, when the temperature up to 400 °C, the more mass loss because of the decomposition of the CNSL compound. The mass transformation was occurred, so that the mass decreasing was appeared in the STA spectras (Figure 3). The quantity of mass loss has been retyped in Table 3.

![Simulant Thermal analysis of CNSL](image)
Table 3. The mass loss of CNSL during temperature treatment

| Temperature (°C) | Mass (mg) % | Δ mass (%) |
|------------------|-------------|------------|
| Room temperature |             |            |
| 34               | -3.5        | 6.2        |
| 145              | -2.7        |            |
| 350              | -3.0        | 40.3       |
| 500              | -4.3        |            |

3.1. Tensile strength

There are two specimens generated, those are specimen of Formula 1 (F1) and Formula 2 (F2) by the different amount of resin in each Formula. The tensile strength measurement results are F1= 600 N and F2= 900 N, respectively. In addition, the elongation of F1=1.98 and F2=2.56. The higher mechanical properties results were affected by the amount of CNSL resin. Resin can bind to the filler materials such as Al₂O₃, Fe₂O₃, SiO₂, MgCO₃, BaCO₃ used in the composites preparation. The composition of each formula was showed in the Table 1. Specimen of F2 have more resin content that F1. The more resin, the more effective bonding occurs among the materials.

Figure 4. Pressure strength test result of extended formula 2

Since formula 2 has better tensile strength result then it was derivated to 4 extra formulas. The pressure strength of those formulas were tested using UTM machine and showed good results. The best pressure strength result was from formula with 20% CNSL resin content, reaches more than 20.000 N. The excellent pressure strength was supported by the hardness property of CNSL resin so that produce better mechanical property of composite based brake pads.
Figure 5. Scanning Electron Microscopy analysis of brake pads composite microstructure of Formula 1 (a) and Formula 2 (b)

Scanning electron microscopy analysis showed in figure 4 for determining morphological appearance of composite shows excellent blend in microstructure scale of fibre glass and filler materials in each formula. It proves that the addition of CNSL resin improves physical bonding among all of composite components.

4. Conclusion
Cashew nut shell liquid (CNSL) have been used as a substituent of phenolic resin. The CNSL compound of cardanol, acid cardanol and cardol can act as a binder in the brake pads composite preparation due to the functional group in their compound. Infrared test showed the presence of hydroxyl groups belong Cardanol. The CNSL has high stability in temperature under 400 °C, proved by the small decrease of its mass in the temperature range of 0 - 350 °C. The addition of CNSL resin also improve mechanical properties of brake pads composites proven by higher tensile strength, elongation and excellent pressure strength of formula 2, 900 N, 2.59 MPa and 20,000 N respectively.

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