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Performance Characteristics of Nano Palm Shell Ash (NPSA) in Asphalt Mixture

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ABSTRACT

One innovation in creating new materials that have superior properties compared to large-sized materials is to use nanotechnology. The uniqueness of nano materials is that the smaller the size of the material, the greater the surface area and performance characteristics of the material in the asphalt mixture. This research develops nano technology in asphalt pavement construction by making nano material from palm shell ash waste. The aim of this research is to determine the effect of adding palm shell ash nano material as a substitute for asphalt in the AC-WC mixture. The research method was carried out by testing the morphological characterization of the palm shell ash nano material using X-Ray Fluorescence (XRF) testing and Scanning Electron Microscope (SEM) testing, then continuing with testing the characteristics of the mixture using the Marshall testing method. The nano material used is palm shell ash material obtained from palm shell burning waste originating from Riau which is then processed into Nano Palm Shell Ash (NPSA) material using a ball mill. The asphalt used is Pen 60/70 asphalt produced by Pertamina. The use of NPSA material in asphalt modification with NPSA variations of 1%, 2% and 3% can improve the performance of marshal characteristics compared to conventional asphalt mixtures. It can be seen that the stability, flow, VFA and MQ values increase with increasing NPSA percentage in asphalt. Meanwhile, the VIM and VMA values decreased along with the increase in the NPSA percentage in asphalt. In addition, increasing the percentage of NPSA in asphalt can reduce the use of optimum asphalt content compared to conventional asphalt mixtures. Utilizing palm shell ash waste is the best alternative for improving the performance of asphalt in mixtures and is environmentally friendly and economical.

1. Introduction

Oil palm is the largest plantation in Indonesia. Riau is the largest palm oil producer in Indonesia, namely 8.96 million tonnes of 45.121 million tonnes of palm oil production in Indonesia with an oil palm area of 3.49 ha of the 16,833 ha of palm oil area in Indonesia based on National Leading Plantation Statistics data 2021-2023 (2022) . With the large amount of palm oil production, the waste

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produced is also increasing. The increasing amount of Palm Shell Ash is an environmental problem [1-5]. Utilizing palm shell ash waste is one way to overcome the problem of environmental pollution. Solid waste from palm shells which produces palm shell ash is used to modify asphalt by changing palm shell ash material into nano material. In addition, palm shell ash has a dominant silica (SiO2) content to be used as an economical and environmentally friendly filler. Modification of asphalt with natural materials has been widely carried out, such as modification of asphalt with natural materials, natural rubber, asbuton, zeolite and so on [6-19]. Current research focuses more on waste materials, reducing asphalt mixing temperatures, and energy replacement such as recycled RAP, crumb rubber, recycled aggregate, biochar, palm oil fuel ash, and bio-based binders can help reduce the environmental impact of production and maintenance of asphalt pavements as well as lower costs and improved performance of the mixture when compared with conventional materials [20-23]. Waste materials, such as palm fuel ash, rice husk ash and coconut shell rattan, have been utilized as additives in composite materials, and some waste materials have been used as nanomaterials [24-30], producing satisfactory results with improved performance. Composite materials are also sustainable structures by reducing waste materials [31-33].

Apart from that, in previous research, processing bio asphalt from coconut shells (BioCS) and BitutechRAP with asphalt binder material pen 60/70 and Aged from the extraction of recycled asphalt pavement (RAP) showed the results that bio asphalt can improve the mechanical performance of asphalt binder aged close to pen. 60/70 as controller [34]. In addition, the use of bioCS as a RA binding rejuvenation agent can be used and research can be continued on a field scale [35]. Apart from that, modified asphalt with nano coconut shells has good strength and quality and biodegradable properties in various composite structures [29,36-38].

Nanomaterials have a very small size, namely less than 100 nanometres. Nanomaterials can be one-dimensional (surface film), two-dimensional (strands or fibres), three-dimensional (particles). In reality, nanomaterials can be single, fused, aggregated or agglomerated with round, tubular and irregular shapes [39]. Nanomaterials can be made in various dimensions as in Figure 1, namely zero dimension (atomic clusters, filaments and cluster assemblies), one dimension (multilayers), two dimensions (ultrafine-grained overlayers), and three (nanophase materials consisting of equiaxed nanometre size grains) [40]

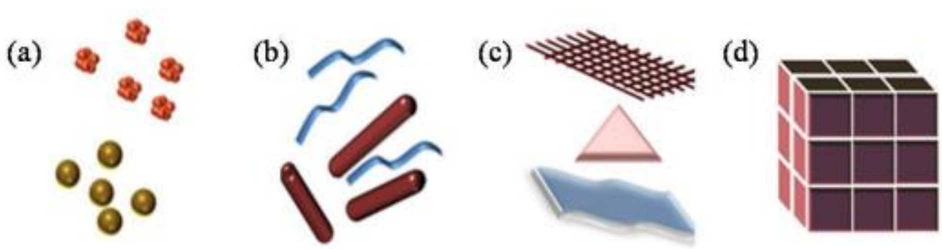


Fig. 1. Classification of Nanomaterials (a) 0D spheres and clusters; (b) 1D nanofibers, and nanorods; (c) 2D nanofilms, nanoplates, and networks; (d) 3D Nanomaterials [35]

Nanomaterials have very fine structures measuring nanometres or one millionth of a meter. The way to form nanoparticles can be done by synthesis using a chemical 'bottom-up' method, namely by uniting or growing atoms obtained from molecular precursors. The bottom-up method requires the stability of the active substance to prevent the formation of micro-scale material. Meanwhile, in the 'top-down' method, nanomaterials are made by separating molecules that gather in large quantities into small ones using grinding and homogenization techniques or by means of physical processes that crush bulk solids (solids) into finer pieces until only a few atoms are formed. which is nanometre in size [40] In general, the formation of nanoparticles is divided into two, namely the bottom-up approach and the top-down approach as in Figure 2.

The bottom-up method is to combine atoms or molecules to form the desired nanometre-sized particles. The method for making nanoparticles consists of several chemical and physical processes, namely:

i. the wet chemical process is a precipitation process such as: colloid chemistry, hydrothermal process, and sol-gel process. This process is carried out by mixing certain amounts of ions and adjusting the temperature and pressure to form insoluble material to form a precipitate. The sediment is collected by filtration or spray drying to obtain dry particles
ii. from-in-place process, there are several methods such as lithography, vacuum deposition process and spray coating. This process is specifically intended for making coating nanoparticles
iii. gas-phase synthesis is controlling the development of carbon nanotubes with a catalytic cracking process in gases full of carbon such as methane.

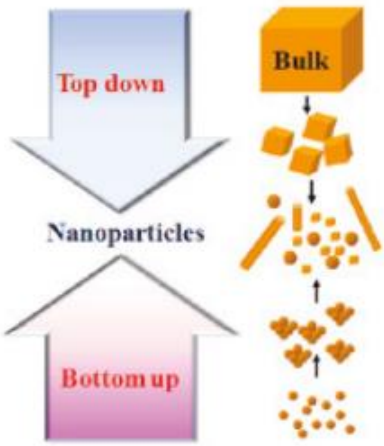


Fig. 2. Top-down and bottom-up nanoparticle synthesis methods [31]

The top-down method is a method of making nanomaterials by destroying large materials into smaller nanometre-sized ones [41,42]. The top-down method has several types of methods such as milling, ultrasonic and laser ablation [43]. In the top-down method, the bulk material is crushed to nanometre size. The top-down method can be carried out using the MA-PM (mechanical alloy powder metallurgy) or mm-pm (mechanical milling powder metallurgy) technique. In the mechanical alloy powder metallurgy technique, the material is crushed until it becomes powder and the particles are continued to be refined. One top-down method that is often used to grind material is using a planetary ball mill. Planetary ball mill technology has the advantage of a relatively short processing time with greater results compared to other machines for reducing particles, so this method is widely used by researchers. The grinding process using a planetary ball mill has the potential to be very profitable whether used to mix materials or reduce particles down to nanometre size.

Modification of asphalt with nanomaterials is one method that can improve the performance of asphalt mixtures because of the large surface area and small size of nanomaterials (1–100 nm). The development of research using nanomaterials is very rapid because of their small size (1–100 nm) and large surface area, which can have long-term effects on road pavement performance [44,45]. Due to their large surface area and small size, nanomaterials show specific characteristics compared to materials in general and show several new properties and extraordinary features that allow them to be applied in the field of asphalt pavement as additional materials [46].

Research that combines nano CaCO3 and Buton Granular Asphalt (BGA) can improve the performance of the asphalt mixture because it has a very small particle size on the nanometre scale and has a regular crystal structure and Nano CaCO3 can strengthen the mixture bonds because it has excellent absorption properties. Apart from that, BGA is a local material which has a very high aromatic and resin content so that it can increase stiffness with sufficient flexibility to withstand traffic loads with mixed variations of 2% and 3% nano CaCO3 and 3% BGA used in the mixture. asphalt [47].

Nanomaterials can be used to develop new pavement materials that can withstand traffic loads and environmental conditions. Nano materials mixed into asphalt can improve the performance of the asphalt mixture, especially in grooves and cracks [48]. Nano coconut shell ash significantly improves the properties and performance of asphalt mixtures and can reduce aging. - In addition, Nano Coconut Shell Ash can produce high adhesion between bitumen and aggregate particles [49]. The characteristics of modified asphalt material can be influenced by several factors, one of which is the size of the filler material. The smaller the particle size, the higher the bond between the particles.

Based on several things related to asphalt mixtures with nano materials, especially the modification of asphalt with palm shell ash nano material as a substitute for asphalt, not much has been done. However, palm shell ash material has been widely studied as a substitute for filler in the asphalt mixture industry which results in the production of better asphalt mixtures with better volumetric properties, stability and durability [50]. Therefore, this research was conducted to identify the performance characteristics of hot asphalt mixtures with nano materials from palm shell ash. Apart from that, this research aims to determine the effect of adding nano palm shell ash material to the AC-WC asphalt mixture. The mixture used in this research is a mixture of 60/70 pen asphalt with Nano Palm Shell Ash (NPSA). NPSA as a potential modifying agent in asphalt binder.

2. Methodology

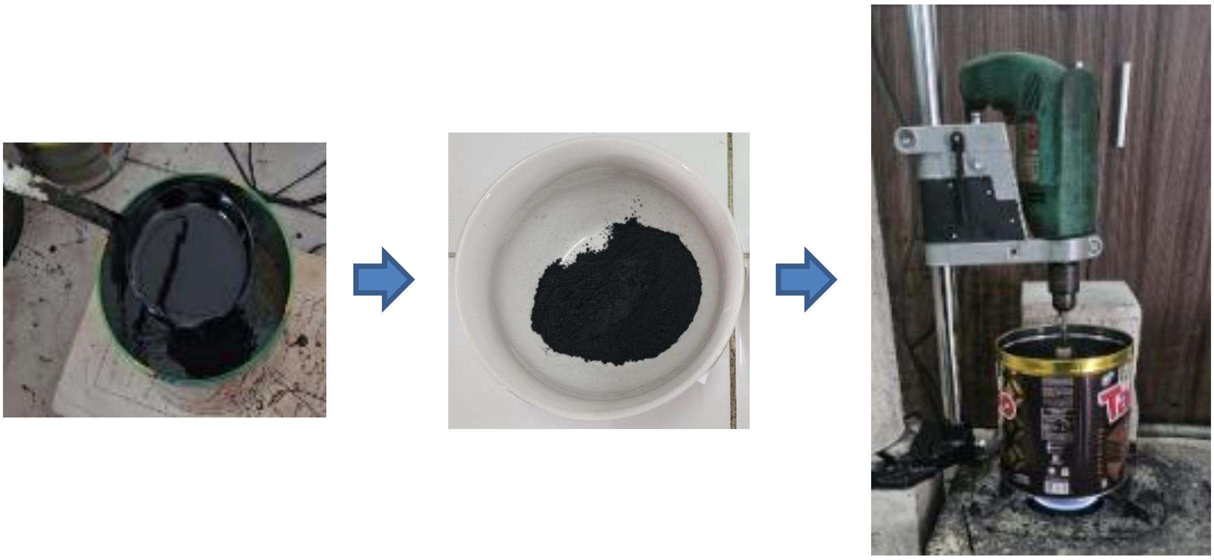
2.1 Material and Methods

The material used in this research is Pertamina Pen 60/70 asphalt, aggregate originating from PT. Riau Mas Bersaudara and palm shell ash material comes from the PT Palm Oil Factory. Jatim Propertindo in Siak Regency, Riau Province. Palm shell ash can be used as an economical and environmentally friendly filler. Palm Shell Ash is ash that comes from fruit shells and fibres that have been ground and burned at a temperature of 500 to 700 ^{0}C in a boiler furnace. Nanoparticles can be made using several methods such as: sol-gel reaction, sonochemical, coprecipitation [51].

The manufacture of palm oil boiler ash nanoparticles was carried out using a ball mill and coprecipitation method [52-60]. Researchers chose to use the coprecipitation method and the ball mill method because they are cheaper and simpler. This method is easy to do, can be done continuously, besides that the materials and working method are simpler. The coprecipitation process is carried out at low temperatures (70^{0}C), it is easy to control the particle size, so the time required is relatively short. The coprecipitation method is a method used to synthesize polymer powder by adding HCL as a solvent and NH4OH as a precipitator to produce nanoparticles.

(a) (b) (c) (d)

Fig. 3. (a). palm fruit (b) palm shell (c) palm shell ash (micro) (d) nano palm shell ash



(a) (b) (c)

Fig. 4. (a) Asphalt pen 60/70 (b) NPSA (c) Asphalt Mixing Process with NPSA

3. Results and Discussion

X-Ray Fluorescence (XRF) testing aims to analyse the chemical composition and concentration of elements contained in palm shell ash using spectrometric methods. The analytical method used is quantitative analysis which is carried out to determine the concentration of elements in a material. The principle used in the process of determining an element or constituents is based on the interaction of X-rays with a sample. Based on the results of the X-Ray Fluorescence (XRF) test as in Figure 5, this palm shell ash material contains a dominant silicon dioxide (SiO2) compound of 69.81%.

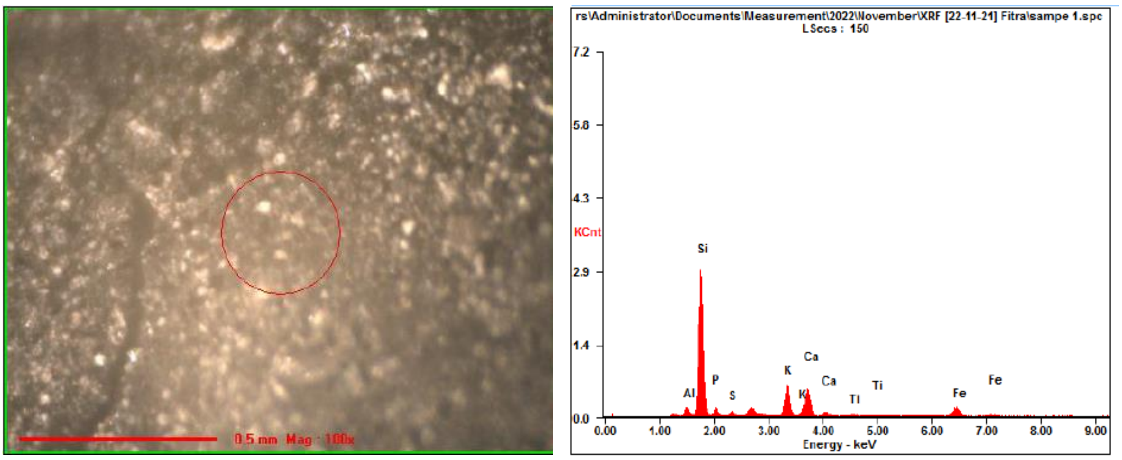


Fig. 5. Dominant compound content of palm shell ash material based on XRF testing

The silicon dioxide (SiO_2) compound that is dominant in palm oil waste is also produced in palm oil waste clinker powder (WPOCP) [50]. The results of XRF testing on palm shell ash material are presented in Table 1. The use of silica from Palm Shell Ash as a substitute for asphalt can overcome environmental problems because the amount is quite abundant and easy to obtain.

Table 1
Dominant Compound Content of Palm Shell Ash Material Based on XRF Testing

No.	Compound	Proportion (%)
1.	Silikon dioksida (SiO_2)	69,81%
2.	Aluminium oksida (Al_2O_3)	6,36%
3.	Kalsium oksida (CaO)	5,80%
4.	Besi (III) oksida (Fe_2O_3)	2,45%
5.	Kalium oksida (K_2O)	6,72%
6.	Sulfur Trioksida (SO_3)	2,00%
7.	Difosfor Pentaoksida (P_2O_5)	6,42%
8.	Titanium Dioksida (TiO_2)	0,44%

From the results of SEM photos with a magnification of 10,000 times, it can be seen that nano-sized Palm Shell Ash has a granular morphology with a more uniform and even size. Meanwhile, Palm Shell Ash that passes through the 400 sieve has an irregular grain shape and the surface tends to be round, graded, non-uniform and uneven as seen in Figure 6. If you look at the SEM photo of palm oil clinker powder (WPOCP), it also shows the morphology of the material structure. with an uneven and scaly surface structure of pores [50]. It can be concluded that palm shell ash nanotechnology can change the quality of palm shell ash. Palm shell ash morphology. The asphalt mixture used in this research is the Asphalt Concrete Wearing Course (AC-WC) mixture which consists of several modified types of asphalt mixture using Asphalt Pen 60/70. The design method and provisions for mixed characteristics refer to the 2018 General Specifications for Road and Bridge Construction Works (Revision 2) of the Directorate General of Highways

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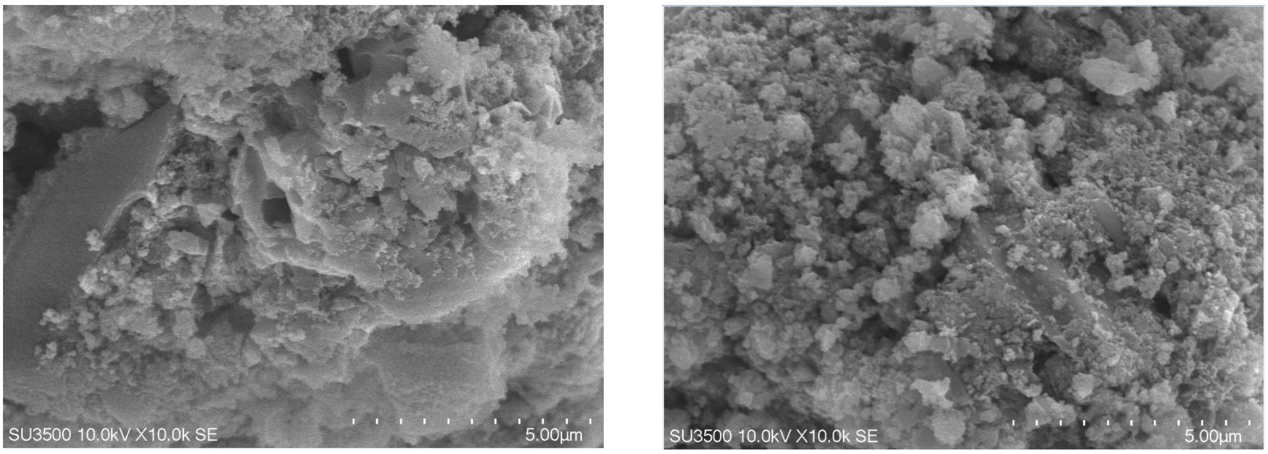

(a) (b)

Fig. 6. SEM photo results of Palm Shell Ash material with 10000 times magnification, (a) PSA 400 (b) NPSA

The use of NPSA material in asphalt modification with 1%, 2%, and 3% NPSA variations can reduce penetration values, increase soft points and reduce ductility values. In addition, the addition of NPSA by 1%, 2%, 3%can also reduce the mixing temperature by 5°C, 18°C, and 35°C and decreases the compaction temperature by 5°C, 28°C, and 45°C from asphalt control (Pen 60/70). It can be concluded that the asphalt modification of NPSA is a warm asphalt (Warm Mix Asphalt/ WMA) because it can be produced at a temperature of 35°C lower than the hot mix (Hot Mix Asphalt/ HMA) [24].

Through testing the performance of this asphalt mixture, it is hoped that the effect of asphalt modification with Nano Palm Shell Ash (NPSA) on asphalt mixtures can be known. The research stages carried out are determining the planned gradation and weight of each mixture and Marshall testing to obtain KAO for each type. mixed AC-WC design.

The aggregate used is the result of processing (breaking) from PT. Riau Mas Bersaudara in the Kampar Riau area. The aggregate size of the stone crushing machine results is grouped into 4 fractions, namely; Fraction 2-3 (aggregate size 20 mm to 30 mm), fraction 1-2 (aggregate size 10 mm to 20 mm), fraction 0.5 – 1 (aggregate size 5 mm – up to 10 mm), and fraction screen or stone ash (aggregate size smaller than 5 mm). The aggregate used as a constituent of the asphalt mixture must have characteristics that are within the range of required values according to the specifications used as a reference. Next, mix gradation planning is carried out to obtain suitable proportions of materials used in the mixture. The mixture gradation curve can be seen in Figure 7.

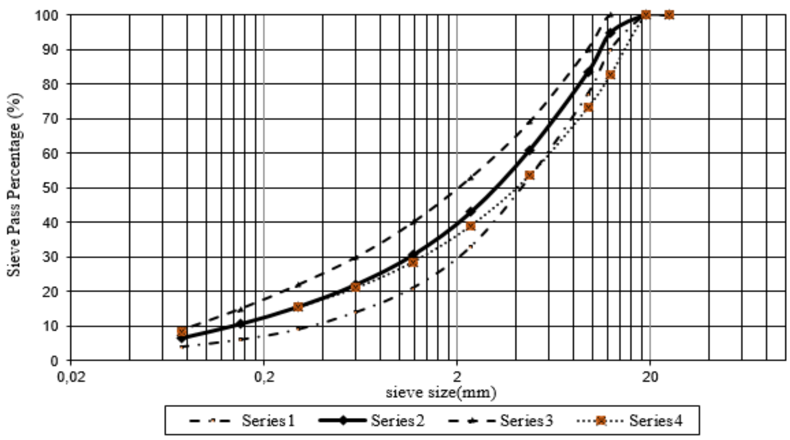

Fig. 7. Gradation of asphalt concrete mix between layers (AC-WC)

Based on the results of aggregate characteristic testing, it can be seen that the aggregate used in the research meets the requirements specified in the 2018 General Specifications for Road and Bridge Construction Works for Highways and Bridges (Revision 2) of the Directorate General of Highways, so it is suitable for use in research.

Table 2
Basic characteristics of pen 60/70 asphalt

Properties	Unit	Value	Specifications
Penetration (25°C)	0,1 mm	62,3	60 – 70
Viscosity (135°C)	cSt	446,7	Min 300
Softening Point (°C)	°C	50,5	Min 48
Ductility (25°C)	cm	>100	Min 100
Flash Point (°C)	°C	245	Min 232
Spesific Gravity		1,041	Min 1

Figure 8 (a) explains the increase in stability of the asphalt mixture with the addition of nano palm shell ash. This shows that the durability of the asphalt mixture with the addition of nano palm shell ash is better when compared to the HMA Kontol Pen 60/70 mixture. Apart from that, by adding nano palm shell ash content up to 3%, the resulting stability value increased by 4644.757 kg when compared to using 1% nano palm shell ash with a stability value of 3390.333 kg. Referring to previous research, asphalt modification with palm oil clinker powder (WPOCP) also experienced an increase in the stability value by adding the percentage of palm oil clinker powder (WPOCP) in the asphalt and the optimum value for adding WPOCP to the asphalt was obtained at 6% WPOCP [50]. In addition, research reviews the effect of palm kernel shells (PKS) and their calcined nanomaterials (CN-PKS) as aggregates on volumetric and Marshall Properties. The stability value and optimum air cavity percentage were obtained at 20% [61].

Furthermore, research using palm kernel shells (PKS) was used as a partial replacement for fine and coarse aggregates in asphalt. Crushed palm shells (CPKS) and PKS were added as much as 20, 40, 50, 60 and 80% of the total aggregate weight to replace some of the fine and coarse aggregates in asphalt concrete. CPKS has a stability value of 1,033 kg at a variation of 60%, while PKS has a stability value of 2,860 kg at a variation of 20%. Palm kernel shells can be used as an alternative coarse aggregate material for light, medium and heavy traffic roads, while 20% of crushed palm shells can be used as fine aggregate on heavy traffic roads and 60% on medium traffic roads [62].

The performance of Charcoal Coconut Shell Ash (CCSA) in Asphalt Mixtures in Long-Term Aging in this study produced asphalt concrete that was durable and had high serviceability using CCSA 2% to 4% of the asphalt weight [63]. Figures 8 (b) and (c) explain that as the percentage of NPSA in the mixture increases, the flow value also increases with increasing asphalt content, while VMA decreases with increasing percentage of NPSA and asphalt content in the mixture. Figure 8 (d) explains that there are differences in the size of the voids in the mixture. From this value, it can be seen that there is a decrease in the value of voids in the mixture (VIM) along with increasing use of asphalt content. The control mixture produced a greater VIM value when compared to the mixture with the addition of palm shell ash nanomaterial. This shows that the palm shell ash nano material is able to fill in the gaps in the mixture. Apart from that, when the nano palm shell ash content was added at 3%, the resulting VIM value decreased compared to using 1% nano palm shell ash. Previous research using nano silica material also resulted in a decrease in the value of voids in the mixture (VIM) when adding nano silica and an increase in the use of asphalt content in the asphalt mixture. This shows that the addition of silica nanomaterials can fill the gaps in the mixture [59]. Apart from that, research by adding BGA with CaCO3 nano material will also increase the VIM value to a smaller extent [38]. The lower the VIM value, the higher the risk of the mixture bleeding and the higher the risk of the mixture decreasing its durability. Figure 8 (e) explains that the VFA value increases with increasing NPSA and asphalt content in the mixture. The MQ value also experiences the same thing as Figure 8 (f).

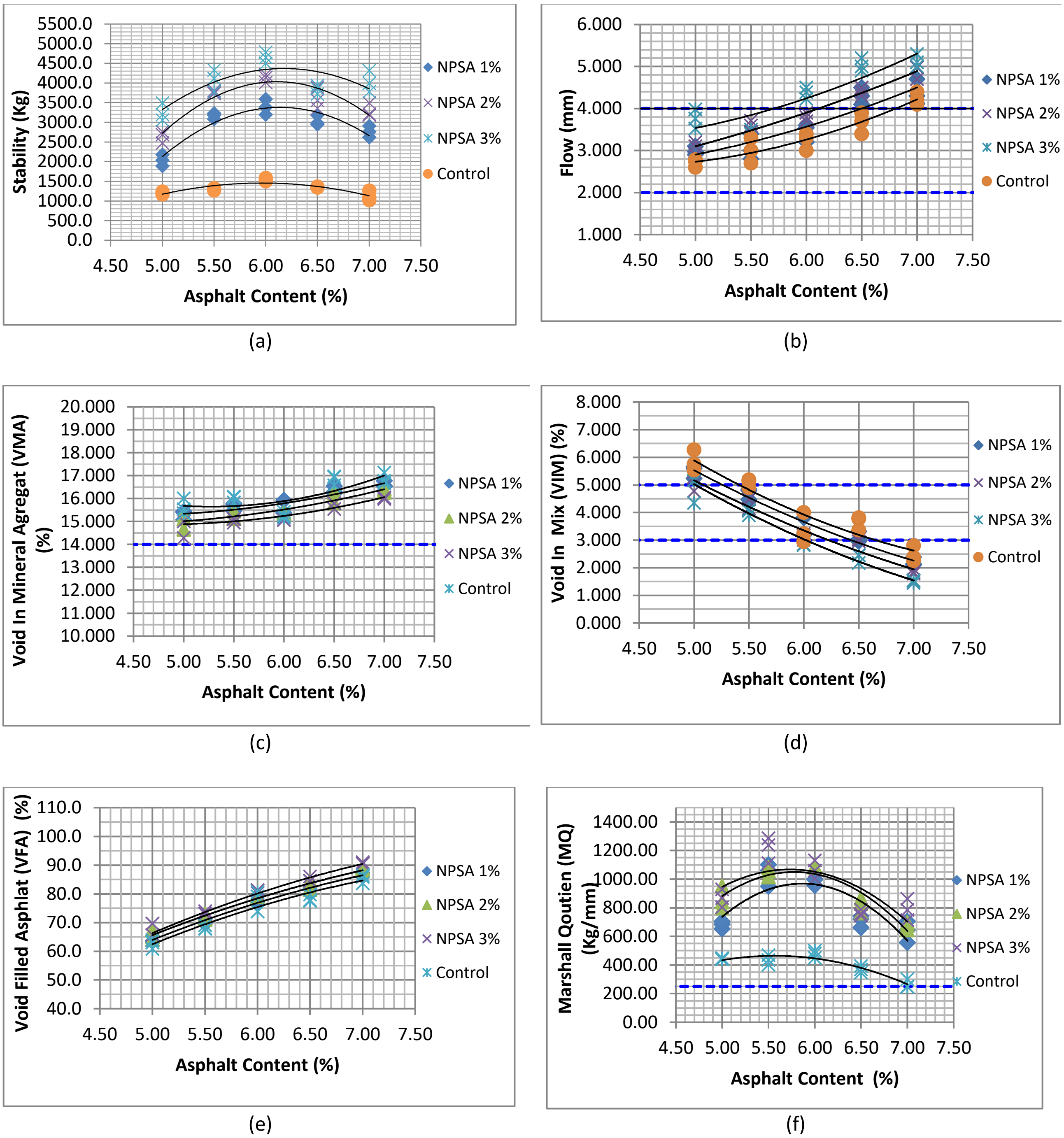

Fig. 8. Characteristics of Palm Shell Ash Nano Modified Asphalt Mixtures in Marshall Testing (a) Stability of variations in asphalt content (b) Flow from variations in asphalt content (c) Void in Mineral Agregat from variations in asphalt content (d) Void in Mix from variations in asphalt content (e) Void Filled Asphlat (VFA) from variations in asphalt content (f) Marshall Qoutien (MQ) variations in asphalt content

Figure 9.The addition of NPSA to asphalt can reduce the optimum asphalt content to 5.35% with a decrease of 0.65% from the asphalt controlpen 60/70 content so that the need for asphalt in the mixture decreases. The performance of the asphalt mixture with the addition of Nano-Charcoal Coconut Shell Ash (NCA) also increased compared to the control asphalt mixture. The optimum NAC content was obtained at 6% from various NAC variations which can improve the technical properties of the asphalt mixture. This is due to its optimal density and stability; the highest tensile strength is achieved at 1288 kPa which increases the internal resistance of the mixture to cracking. The ability

of the asphalt mixture to return to its original state after being loaded is demonstrated when it is resilient [64]. palm oil clinker fine (POCF) as an asphalt modifier through material characterization tests produces more improvements in the conventional properties of asphalt such as reduced penetration, increased softening point. Optimum POCF levels were obtained at 6.3% POCF variation [65].

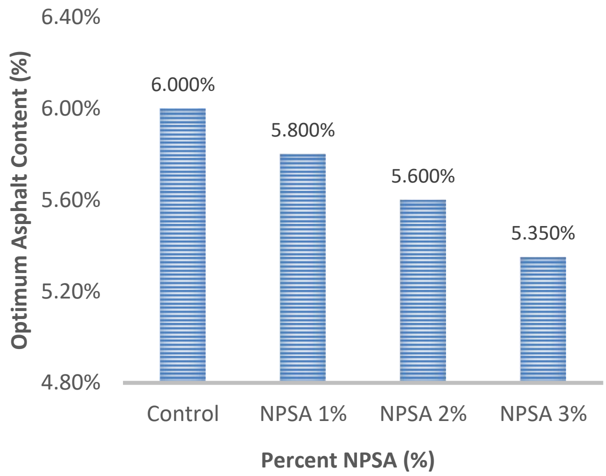

Fig. 9. Optimum asphalt content with NPSA variations

4. Conclusion

The aim of this research is to identify the performance characteristics of hot asphalt mixtures with nano materials from palm shell ash and to determine the effect of adding nano palm shell ash nano materials to AC-WC asphalt mixtures. The mixture used in this research was a mixture of 60/70 pen asphalt with Nano Palm Shell Ash (NPSA). NPSA as a substitute for asphalt in asphalt binder. This research provides benefits for environmentally friendly road pavement construction.

The use of waste from palm shell ash is the best alternative to overcome environmental pollution problems. Palm shell solid waste which produces palm shell ash is used to modify asphalt by changing palm shell ash material into nano material. Palm shell ash has a dominant silica ($SiO2$) content of 69.81% so it can be used as an economical and environmentally friendly substitute for asphalt.

Increase in stability in the asphalt mixture with the addition of nano palm shell ash. This shows that the durability of the asphalt mixture with the addition of nano palm shell ash is better when compared to the HMA Kontol Pen 60/70 mixture. Apart from that, when the nano content of palm shell ash was added up to 3%, the resulting stability value increased by 4644.757 kg when compared to the use of 1% nano palm shell ash with a stability value of 3390.333 kg. decrease in the value of voids in the mixture (VIM) when the use of asphalt content is increased. The control mixture produced a greater VIM value when compared to the mixture with the addition of palm shell ash nanomaterial. This indicates that the palm shell ash nano material can fill the voids in the mixture. Apart from that, when the nano palm shell ash content was added to 3%, the resulting VIM value decreased compared to using 1% nano palm shell ash.

The performance of NPSA modified asphalt mixtures has increased compared with control asphalt mixture pen 60/70. The addition of NPSA to asphalt can reduce the optimum asphalt content to 5.35% with a decrease of 0.65% from the asphalt controlpen 60/70 content so that the need for asphalt in the mixture decreases. This shows that the 3% NPSA asphalt mixture produces a strong bond between materials compared to the control sample. Therefore, the performance of the asphalt mixture is significantly improved through additional NPSA 3%.

Based on the results of the study, to help achieve sustainability and improve performance in the coming years, the use of palm oil waste is a sustainable alternative as an environmentally friendly and economical material. This research is also recommended to investigate long-term performance under various environmental and traffic conditions. It is also recommended to conduct research on the effect of NPSA on asphalt stiffness modulus and resistance to permanent deformation and fatigue cracking

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