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Microstructure and physical properties of nano charcoal ash as binder

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Waste coconut shell (CS) was used to produce nano charcoal ash (NCA) as a potential modifier material in an asphalt binder. This study focused on the microstructural and physical properties of NCA. Thermogravimetric analysis and derivative thermogravimetric analysis (TGA/DTA), field emission scanning electron microscopy (FESEM), X-ray fluorescence, particle size analysis (PSA), penetration tests, softening point tests and dynamic shear rheometer (DSR) tests were performed. The TGA/DTA results revealed 490°C to be a suitable CS burning temperature to form carbon and to reduce impurities. The morphology determined by FESEM showed that charcoal CS presents a smooth, porous and irregular shape. The carbon content on the surface of the material was 77.6%, as indicated by energy-dispersive X-ray spectroscopy. PSA showed that the optimum size of the charcoal CS obtained after several grinding cycles was 148 nm. Test results indicated that adding NCA from coconut shell to bitumen improved the binder stiffness up to 47% and significantly increased the softening point up to 12% compared with virgin binder. The DSR test revealed that the optimum size of NCA enhanced the bitumen by increasing the resistance to rutting until a temperature of 76°C was reached, prior to failure at a temperature of 82°C.

1. Introduction

In Malaysia, 95% of the pavement is constructed from asphaltic concrete (Che Mat *et al.*, 2014). Proper bonding between the bitumen and the aggregate is very important to ensure that construction using asphaltic concrete is strong and durable, provides a smooth surface and can accommodate traffic loadings adequately. However, due to increasing traffic volume, greater loads and pressures are applied on asphalt pavements by various vehicles, including heavy lorries and trucks. In addition, its susceptibility to high temperature leads to changes in the properties of bitumen, which cause pavement distress such as rutting and fatigue cracking, and reduces the performance of asphalt pavements (Hainin *et al.*, 2013, 2014, 2015).

These are the reasons why modifiers and additives are being introduced into the asphalt binder. The main advantages of the modified binder in terms of engineering factors are that the properties of the bitumen will be improved and there will be a high resistance to rutting and fatigue cracking and a decrease in temperature susceptibility. In terms of environmental and economic factors, the waste materials and the maintenance costs, respectively, can be reduced. Numerous

modifiers have been used in previously published studies; these include polymers, industrial by-products, waste materials and agricultural waste materials. In addition, the potential of agricultural waste materials such as palm oil fuel ash, palm kernels, rice husk ash and coconut shell (CS) as bitumen modifiers has been more extensively explored in the current concrete and asphalt pavement industries. This is a result of the high increment in the disposal of natural resources. Thus, rather than throwing them away, it is better to reuse them in other applications, such as modifiers in asphalt binders. Through this alternative, not only can wastes be reduced but they can also be used to enhance the properties of asphalt binders. From all the research on using agricultural waste materials, it seems that CS has so far been very little used as a modifier in asphalt binders. Based on previous research, CS has potential as a filler in composite structures (Agunsoye *et al.*, 2012, 2014; Husseinayah and Zakaria, 2011; Kumar and Kumar, 2012; Madakson *et al.*, 2012; Sapuan *et al.*, 2003; Sarki *et al.*, 2011; Singh, 2013) and as an aggregate in concrete and asphalt mixtures (Gunasekaran, 2011; Gunasekaran *et al.*, 2011, 2012, 2013; Jeffry *et al.*, 2016; Norhafizah *et al.*, 2016; Ramadhansyah *et al.*, 2016). Coconut is one of the crops

that grows in tropical countries such as Malaysia, Indonesia, Philippines, Thailand and India. According to FAOStat (2015), Malaysia is the tenth largest coconut grower in the world with a production of 624 727 t of coconuts. In addition, coconut is the fourth largest crop in Malaysia after palm oil, rubber and paddy (FAOStat, 2015). The Malaysian Agricultural Research and Development Institute has conducted extensive research and development studies involving coconut (Sivapragasam, 2008). CS is widely discharged by various industries, thereby leading to environmental pollution.

There are numerous coconut-based products being produced such as coconut oil, desiccated coconut, coconut milk powder, CS charcoal and activated carbon (Sivapragasam, 2008). Of all the products, charcoal CS is widely produced to be used in many types of applications and has many benefits. Commonly, charcoal is known as a black material containing carbon as the main chemical component. It is usually produced by burning or heating wood without air in an enclosed space. Charcoal is usually used as a fuel and it is recognised as a 'green' material because it is safe to use. The Food and Drug Administration has stated that plain charcoal, which is safe and effective, is categorised as category 1 (Nath Giri, 2015). Charcoal CS has been used in various research fields because it is efficient, environmentally friendly and economical, and it has the potential to enhance the properties of composite materials (Ouyang *et al.*, 2013; Pukird *et al.*, 2009; Rampe *et al.*, 2011; Read and Whiteoak, 2003).

Recently, nanotechnology has drawn the interest of researchers from various fields. Generally, nano is a scale of size in the metric system which is one-billionth of a metre. Figure 1 shows the scale of various items from the milliscale to the nanoscale. It can be seen how small the nanoscale is compared with other scales. The nanoscale is in the range of 0.1 μm or 1000 nm to 0.1 nm. However, the novel and unique properties of materials are developed at the nanoscale range of 1–100 nm due to the small size (Hornyak *et al.*, 2008). Therefore, nanotechnology is a study that is concerned with materials at a nanometre size of 1–100 nm. The International Standards Organization states that a nanoparticle is a particle that has all three dimensions in the range of 1–100 nm (Shatkin, 2012). Nanomaterials are formed from nanoparticles. Nanostructured materials, on the other hand, comprise one-nano-dimensional (nano thin films), two-nano-dimensional (nanotubes and nanofibres) and three-nano-dimensional nanomaterials (nanopowders and nanoparticles) (Pokropivny *et al.*, 2007). At the present time, nanomaterials such as nanoclay, nanosilica and nanocarbon are introduced frequently in the pavement engineering field.

The unique properties of nanomaterials can be attributed to their nano-size. The factor that makes the nanoscale unique

compared with other scales is that it has a larger surface area than the same volume of material in a larger size (Calicut University, 2013; EHS, 2016; Pokropivny *et al.*, 2007). A small particle size leads to a large surface area and the large surface area can cause exposure to more collisions and increase the frequency of collisions. Hence, the rate of reaction will increase and the material will become more chemically reactive. In pavement engineering, the interfacial forces between the nanomaterials and the asphalt binder will be enhanced, which will increase the strength and hardness of the materials. It is important to control their composition, size and structure (Calicut University, 2013). This is to ensure that the desired properties of nanomaterials can be achieved.

A few past studies that focused on the performance of asphalt binders modified by nanomaterials in terms of physical and rheological properties have been reviewed. Alhamali *et al.* (2015) added nanosilica in asphalt binder PG 76 and the results showed that the penetration and softening point values were decreased and increased, respectively. Meanwhile, the complex modulus (G^*) was decreased except for the 6% nanosilica addition. The overall results indicated that 6% of nanosilica was the optimum content to improve bitumen in terms of rutting and fatigue cracking. Research done by Yao *et al.* (2013) showed that adding nanosilica in bitumen PG 58 leads to a decrease of viscosity. The complex modulus (G^*) of the nanosilica modified binder was decreased excludes the PAV aging sample at temperature of 13°C in which the G^* was increased. Meanwhile, Jamshidi *et al.* (2015), Yao *et al.* (2012) and You *et al.* (2011) reported that the incorporation of nanoclay in asphalt binder showed that non-modified nanoclay (NMN) had higher viscosity compared with polymer modified nanoclay (PMN) and control binders. With regard to dynamic shear rheometer (DSR) testing, Yao *et al.* (2012) found that the complex shear modulus (G^*) of NMN and PMN were higher and lower than the control binder, respectively. However, from the perspective of dissipated work per load cycle, PMN can improve the resilience to high temperature for unaged, short-term aged and long-term aged binders because they have an enhanced ability to recover compared with NMN binders.

In addition to the above-mentioned studies, the utilisation of nanocarbon powder and nanorubber powders in asphalt binders has been investigated by Yao *et al.* (2011). Different percentages of the nanomaterials were used in bitumen 60/80. The penetration and softening point tests were decreased and increased, respectively. Shafabakhsh and Ani (2015) used nano-titanium dioxide and nano-silicon dioxide in bitumen PEN 60/70 and the mixtures used natural aggregates with 50% steel slag. Based on the binder properties test, the penetration and softening point values were decreased and increased, respectively. The viscosity also increased and the DSR showed that the modified bitumen had higher resistance to rutting.

Figure 1. Scale of various objects (Nanohub, 2012)

Carbon nanofibres were utilised by Khattak *et al.* (2012) in three types of bitumen and binder properties tests were conducted. The results indicated that the carbon-nanofibre-modified bitumen showed an improved viscoelastic response and resistance to rutting. Simultaneously, fatigue life was increased.

Based on past studies, nanomaterials are able to improve the properties of the conventional asphalt binder. It is therefore the aim of this study to investigate the production of nano charcoal from CS as a potential modifier in asphalt binders. The characteristics of nano charcoal ash (NCA) from CS waste are explored in terms of the microstructure of the charcoal and the physical properties of the NCA in the asphalt binder.

2. Materials and methods

2.1 Materials

The materials used in this study are described in the following subsections.

2.1.1 Bitumen

Bitumen PEN 60/70 from Shell, Malaysia was used. The physical properties are shown in Table 1.

2.1.2 NCA CS

2.1.2.1 CHARCOAL PRODUCTION

Figure 2 shows the processes used to produce NCA. First, the collected waste CS from Peter Haw Enterprise, Melaka, Malaysia was cleaned by removing the excessive coconut

meat and fibrous husk. The CSs were then crushed using a crusher machine prior to the burning process, as shown in Figure 2(a). The CSs were burned in a furnace at a temperature of 450°C for 5 min to produce charcoal with high carbon content and to reduce the impurities in the raw CS. The sufficient amount of CS that can be burned in a furnace using a ceramic bowl was about 30–50 g (as shown in Figure 2(b)). Hence, after several trials, 5 min were enough to turn the CS into charcoal to prevent excessive burning of the CS as well.

2.1.2.2 GRINDING PROCESS

Subsequently, charcoal CS with a size of 75 µm was fed into the ball mill and was subjected to five different grinding times, which were NCA1, 2, 3, 4 and 5. The charcoal was ground to form charcoal powder with a nanoparticle size (Figure 2(c)). The virgin binder as the control sample and the non-grinding charcoal ash sample designated as NCA0 were compared with the ground samples (NCA1 to 5) in the bitumen properties and rheological tests. Table 2 provides descriptions of each sample.

2.2 Methods

2.2.1 Microstructure test

Microstructure tests to analyse the thermal properties and morphology of the CS and charcoal CS were carried out.

- (a) Thermogravimetric and derivative thermogravimetric analysis (TGA/DTA) (Figure 3(a)): Thermogravimetry

Table 1. Physical properties of bitumen 60/70

Penetration at 25°C: dmm	61.7
Softening point: °C	46.5
Rutting parameter, $G^*/\sin \delta$ at 64°C: kPa	1.19

analyser model STA 8000 was used to perform TGA/DTA analysis. The sample was heated at a heating rate of 20°C/min from 28°C to 900°C under nitrogen gas protection.

- (b) X-ray fluorescence (XRF): The chemical compositions of the CS and charcoal CS were examined using XRF. The materials were analysed in the form of powder <75 µm. This test was carried out at the Universiti Sains Malaysia, Penang, Malaysia.
- (c) Field emission scanning electron microscopy (FESEM) (Figure 3(b)): The morphology analysis was performed by FESEM model Hitachi SU8020 with elemental analysis by energy dispersive X-rays. The sample was coated with gold prior to surface analysis.
- (d) Particle size analysis (PSA): The average particle size of the ground charcoal (NCA1 to 5) was obtained using a particle size analyser by the technique of dynamic light scattering. This instrument can measure particle and molecule sizes ranging from 20 nm to 2000 µm.

2.2.2 Bitumen physical properties test

Bitumen physical properties tests on the nano charcoal CS-modified bitumen were conducted as follows.

- (a) Mixing method: All the samples in Table 1 were used to replace 30% by weight of bitumen 60/70. The mixing process was conducted using a high-shear mixer at speeds of 1500 r/min for 60 min at a temperature of 180°C. These parameters were chosen based on past studies to ensure adequate mixing between NCA and bitumen to produce a homogeneous binder.
- (b) Penetration test: The penetration test was used to check the consistency of the bitumen. This test was carried out according to ASTM D5 (ASTM, 2013). The bitumen was

Figure 2. Processes to form NCA from CS: (a) CS, (b) charcoal CS, (c) nano charcoal CS

heated and poured into a penetration cup prior to testing. The sample was then placed into a water bath for 1 h at 25°C after it was cooled. The penetration equipment was used to perform the test with an applied total load of 100 g for 5 s at a temperature of 25°C.

- (c) Softening point test: This test was performed in accordance with ASTM D36 (ASTM, 2000). The bitumen was heated and poured into two rings and cooled for 30 min. The two rings and two ball centring guides were placed on the ring holder in a liquid bath. Subsequently, 3.5 g of steel balls were placed on each sample and heated. The temperature that made the bitumen touch the base plate was taken, and the mean temperature of the two samples was calculated.
- (d) Dynamic shear rheometer (DSR) test: DSR was carried out according to ASTM D7175 (ASTM, 2015). The test was conducted at temperatures between 46 and 82°C, with increments of 6°C. For the unaged bitumen, a 1 mm thick plate and 25 mm diameter top plate were used. The bitumen sample was sandwiched between two 1 mm thick plates. Stress was applied on top of the sample by the 25 mm diameter top plate, which oscillated at 1.59 Hz, to

measure the maximum stress, maximum strain and time lag of stress and strain. The rutting performance of the asphalt pavements was analysed from $G^*/\sin \delta$.

3. Results and discussion

3.1 Microstructural analysis

3.1.1 TGA/DTA

A TGA/DTA test was carried out to examine the thermal properties of the charcoal. The relationship between TGA and DTA is shown in Figure 4, showing how the CS was formed into the charcoal CS. Three endothermic peaks are shown in the graph, namely, endothermic peaks 1, 2 and 3. As shown in Table 3, endothermic peak 1 occurs at 68.7°C (range 50–110°C) with a weight loss of 2.8%, indicating the loss of moisture from volatile compounds through evaporation (Vargas-Delgadillo *et al.*, 2010).

Another weight loss peak of 4.8% was observed in the temperature range 110–410°C, at endothermic peak 2 at 195°C. This increase was due to the decomposition of the CS components and the initiation of carbonisation through the evaporation of volatile compounds (Vargas-Delgadillo *et al.*, 2010). Hence, the temperature range from 50 to 410°C indicated the devolatilisation process of CS (Ouyang *et al.*, 2013; Vargas-Delgadillo *et al.*, 2010). The endothermic peak 3 at 490°C (range 410–690°C) presented a weight loss of 18.6% due to the decomposition of cellulose, lignin and pentosans, and carbon formation (Ouyang *et al.*, 2013; Vargas-Delgadillo *et al.*, 2010).

At this stage, charcoal CS without volatile compounds was obtained. The decomposition of the components continued at

Table 2. Samples used in this study

Designation	Grinding: h
Virgin binder	—
NCA0	0
NCA1	20
NCA2	30
NCA3	40
NCA4	50
NCA5	60

Figure 3. Instruments used for microstructure test: (a) thermogravimetry analyser; (b) FESEM; (c) PSA

Figure 4. TGA/DTA curves of charcoal CS

Table 3. Weight loss of charcoal CS

Endothermic peak	Temperature range: °C	Weight loss: %	Maximum peak: °C
1	50–110	2.8	68.7
2	110–410	4.8	195
3	410–690	18.6	490

a low rate until a temperature of 900°C was achieved (Ouyang *et al.*, 2013). Based on this analysis, the most suitable temperature for burning CS was 490°C. This value was supported by the research conducted by Ouyang *et al.* (2013) and Zhao *et al.* (2014a, 2014b) where they stated that the optimum pyrolysis temperature was between 400 and 500°C.

3.1.2 Chemical properties

The chemical compositions of the CS before and after the heat treatment were examined to discover the chemical properties of the materials. This test is important to examine the types of chemical elements that exist in CS and charcoal CS, and also to reduce impurities. According to Read and Whiteoak (2003), the major chemical element in bitumen is carbon at 82–88% based on the chemical analysis from various bitumens. Therefore, material with a high content of carbon was expected to be compatible with asphalt binder. Zhao *et al.* (2014a, 2014b) state that various studies have been conducted using carbon-based materials to modify asphalt binder because of the compatibility of both materials.

Table 4 presents the chemical compositions of both CS and charcoal CS. It can be seen that the carbon content of CS

Table 4. Chemical properties

Chemical compositions: %	Coconut shell	Charcoal CS
Carbon (C)	96.20	99.70
Sodium oxide (Na ₂ O)	0.0688	0.0079
Magnesium oxide (MgO)	0.0991	0.0161
Silicon dioxide (SiO ₂)	0.7997	0.0486
Diphosphorus pentoxide (P ₂ O ₅)	0.2579	0.0250
Sulfur trioxide (SO ₃)	0.2158	0.0125
Chlorine (Cl)	0.3513	0.0137
Potassium oxide (K ₂ O)	1.3451	0.0740
Iron (III) oxide (Fe ₂ O ₃)	0.1696	0.0731
Nickel(II) oxide (NiO)	0.0050	0.0012

and charcoal CS is 96.2 and 99.7%, respectively. Both contain a high proportion of carbon. The carbon formation, as explained in Section 3.1.1, led to the increase in percentage of carbon from 96.2 to 99.7%. Meanwhile, the impurities in CS such as silica, iron, potassium, sodium and other elements that exist in the materials were decreased after the burning process. However, it should be noted that the chemical composition according to the Centre for Chemical and Structural Analysis (CCSA) also depended on the CS source – that is, the way the charcoal was prepared and the presence of contaminants.

3.1.3 FESEM

Figure 5 shows the morphology of the CS prior to burning. As shown in Figure 5(a), CS presents packed discrete structures with a length of 15.4 mm and width of 100 µm. In between these structures, pores with sizes of 578 nm to 1.4 µm exist, as shown in Figure 5(b), with an image size of 20 µm. The CS

Figure 5. FESEM images and EDX of CS. (a) CS image at 500 magnification factor; (b) CS image at 2K magnification factor; (c) EDX of CS

surface was rough, with elongated layers and irregularly shaped. The elements detected by energy-dispersive X-ray spectroscopy (EDX) on the surface of the sample were 56.5% carbon, 42.5% oxygen and 1% potassium, as shown in Figure 5(c).

The charcoal CS in Figure 6(a) shows discrete structures but fine surfaces with a length of 16.8 mm. The morphology of the product was of smooth, porous, sharp-edged and flat-shaped particles. The pore sizes ranged from 915 nm to 1.54 μm , as shown in Figure 6(b). The EDX in Figure 6(c) shows a carbon content of 77.6%, oxygen content of 20.2% and 2.2% potassium. This increase in carbon content could be attributed to the high burning temperature employed, which removed surface functional groups and formed a porous surface over the charcoal CS (Ouyang *et al.*, 2013). A porous surface leads to a larger surface area, which generates more interlocking bonding between particles. The rate of absorption and interaction bonding will increase immediately.

The percentages of elements discovered by the EDX were limited only to the surface of the materials. This is the reason why the materials' compositions obtained by X-ray fluorescence (XRF) in Table 2 were different from the EDX results. Furthermore, the compositions were also influenced by the size of the CS and charcoal CS material used for FESEM analysis, which was solid instead of powder, which was the required state for XRF analysis. However, the carbon content was still the highest detected in the materials.

3.1.4 PSA

Based on Figure 7, the particle sizes of the ground samples were >100 nm but <1000 nm. The optimum size was obtained by NCA2, which was 148 nm, where the charcoal had been ground for 30 h. In addition, it can be seen that, as the grinding time was increased, the particle size was increased too. This might be due to the agglomeration that occurred when the optimum time for grinding was exceeded.

Figure 6. FESEM images and EDX of charcoal CS. (a) Charcoal CS image at 500 magnification factor; (b) Charcoal CS image at 2k magnification factor; (c) EDX of charcoal CS

Figure 7. Particle size of ground samples

Figure 8. Penetration values of bitumen modified by NCA

As mentioned earlier, the novel properties of materials were developed at a nanoscale of 1–100 nm. The particle sizes obtained in this study, however, did not achieve a particle size <100 nm, yet remained in the nanometre range as almost all of the samples had a size <1 μm . Throughout this analysis, the method of grinding needs to be modified in terms of many factors, including the grinding times to obtain the desired size of the nanomaterials.

In addition, the effects of these samples on the asphalt binder are investigated in Section 3.2.

3.2 Bitumen property and rheological test

In this section, the virgin binder as the control sample and the unground charcoal ash sample designated as NCA0 are compared with NCA1, 2, 3, 4 and 5.

3.2.1 Penetration test

Figure 8 shows the penetration values of the modified bitumen samples that were compared with the virgin binder as a control sample. Based on the graph, the incorporation of NCAs into the bitumen gave lower penetration values than the virgin binder. The NCA0 showed the lowest penetration value compared with NCA1 to NCA5, which was 30.90 dmm. In this test, the NCA3 showed the lowest penetration value after the NCA0, which was 35.30 dmm. The NCA3 was 14% softer and 47% stiffer than the NCA0 and the virgin binder, respectively. Therefore, 30% replacement by NCA can increase the stiffness of bitumen by half as much again. The internal strength of the bitumen improved as well. Although the NCA0 showed the greatest improvement, becoming too stiff is not good because it will cause a different problem in asphalt pavements. A low penetration value typically leads to high stiffness of the

bitumen. However, if the bitumen is too stiff it will become less elastic and thereby the flexibility of the asphalt pavements is reduced. This can lead to cracking because the asphalt pavement cannot accommodate traffic loading (Astana, 2010). Hubbard and Gollomb (1973) reported that, when penetration occurred between 20 and 30 dmm, cracking could occur. When the penetration was >30 dmm, the bitumen had a high resistance to cracking, when combined with proper mix design and compaction (Brown *et al.*, 2009).

3.2.2 Softening point test

Based on the results shown in Figure 9, it can be seen that the NCA modified bitumen samples have higher softening point values compared with the virgin binder. The NCA3 had the highest softening point value, which was 50.3°C and was 12% higher than the virgin binder. Meanwhile, the lowest softening point value was acquired by NCA5, which was 48.3°C and was 7% higher than the virgin binder. A high softening point indicated that the binder was less susceptible to temperature. Even though the penetration value of NCA0 was better than that of NCA3, in the softening point test, the value was lower than those of the NCA3 and NCA4 by ~2 and 0.4%, respectively. This showed that the phase change of NCA3 modified bitumen to fluid was lowered where the temperature at which the bitumen softens was high. The physical properties of the control sample and modified samples were determined through their consistency. Based on the penetration test, the consistency of the bitumen at the same temperature was determined at a temperature of 25°C, while the temperature at which the bitumen reached the consistency was determined by the softening point value. The penetration index (PI) was therefore calculated to determine the compatibility of the bitumen.

Figure 9. Softening point of bitumen modified by NCA

3.2.3 PI

The PI is used to determine the temperature susceptibility of bitumen, in which the consistency of the softening point is expressed in terms of penetration, by a linear extrapolation of the logarithm of penetration against temperature (Read and Whiteoak, 2003). The PI value can be obtained either by a nomograph or an equation as (Read and Whiteoak, 2003)

$$1. \quad PI = \frac{1951.4 - 500 \log P - 20SP}{50 \log P - SP - 120.14}$$

where P is Penetration and SP is softening point.

Read and Whiteoak (2003) reported that the range of PI is between -3 for highly temperature susceptibility of bitumen and $+7$ for highly blown low-temperature susceptibility (high PI) of bitumen. However, the suitable PI for road construction was between -1 and $+1$ (Brown *et al.*, 2009). A low value of PI, which approaches a negative value, means that the sample has high susceptibility at low temperature, which can lead to cracking. On the other hand, a high value of PI, which approaches a positive value, indicates low susceptibility at high temperature, which leads to high resistance to permanent deformation or rutting. Based on the results in Table 5, the PI for the virgin binder and NCA modified bitumen did not lie within the range from -1 to $+1$. However, NCA1 to NCA4 still lay in between -2 and $+2$ if following the PI range stated by Domone and Illston (2010) for road use. The lowest PI was obtained by NCA0, which was -2.3 . According to Brown *et al.* (2009) the bitumens that had PI lower than -2 were typically susceptible to low temperatures, thereby leading to brittleness and transverse cracking during cold weather. By contrast,

Table 5. PI value

Ground sample	Penetration index
Control	-1.9
NCA0	-2.3
NCA1	-2.0
NCA2	-2.0
NCA3	-1.8
NCA4	-1.9
NCA5	-2.1

the highest PI was gained by the virgin binder, NCA3 and NCA4 with values of -1.9 , -1.8 and -1.9 , respectively. The less negative value showed that the sample had been improved (Hadavand, 2010). The NCA0 approached a more negative value, which meant that the sample was highly influenced by temperature compared with samples NCA1 to NCA5.

3.2.4 Dynamic shear rheometre

The rutting performance of the modified asphalt binders was compared with that of the virgin binder as shown in Figure 10. It can be seen that the modified samples have higher rutting resistance compared with the control sample. In this test, the rutting parameter $G^*/\sin \delta$ was the parameter used to indicate the resistance to deformation of the binder at pavement service temperatures. The control sample resisted the rutting up to the temperature of 64°C with $G^*/\sin \delta$ of 1.19 kPa and then failed at a temperature of 70°C . The sample that could withstand rutting at the highest temperature was NCA2. It resisted rutting at a temperature of 76°C with a rutting parameter of 1.03 kPa, prior to failure at a temperature of 82°C . The other modified samples all failed at the temperature of 76°C , which

Figure 10. Rutting parameter of the modified samples

was higher than for the control sample. This test showed that the modified samples have improved a lot, especially the NCA2-modified bitumen. The reason NCA2 had a higher rutting parameter than the other samples was because of the particle size of the NCA. The particle size of NCA2 was 148 nm, which was the smallest size compared with the other NCAs. Through the DSR, the effects of the particle size in the modification of the bitumen was more obvious than through the consistency tests. It showed that the nanosized particles at almost <100 nm had improved the properties of the virgin binder more than other samples with a particle size <1000 nm. This can be attributed to the large surface area of the particles, which increased the bonding between the particles. The rate of reaction also increased at the same time, and enhanced the rheological properties of the bitumen.

4. Conclusion

The use of waste materials in the nanosize range from 1 to 100 nm has not been investigated in the asphalt binder. The novelty of this research stems from the nanosize itself, which can improve the properties and performance of asphalt binder in a unique way. Based on this study, the XRF test detected the carbon element in NCA, which was 99.7% after the burning process in which carbon was formed at a temperature of 490°C based on the result of TGA/DTA test. Also, the FESEM results showed that charcoal CS presents smoother, more porous and more irregularly shaped particles than CS. In terms of the particle size, the optimum size was obtained by NCA2 with a size of 148 nm. The charcoal CS was ground for 30 h. Meanwhile, the results obtained by the penetration

and softening point tests showed that the modified samples were improved. The PI for NCA1 to NCA4 was still in the range of -2 to +2, which indicated that the samples have high resistance to temperature changes. Nevertheless, the DSR test showed that NCA2 has higher resistance to deformation compared with other modified samples due to its nanosized particles, which approached 100 nm.

It can be seen that different grinding times have affected the particle size of the material. The performance of the modified bitumen has also been influenced by the different sizes of the particles. The method of grinding therefore needs to be adjusted to obtain a particle size of charcoal in the nanoscale of 1–100 nm. At this scale the novel properties of the materials can be obtained. Subsequently, the nano charcoal will be incorporated in asphalt binder and asphalt mixtures. Thorough analysis will be carried out on the performance of the nano charcoal in the asphalt mixture. In addition, the effects of short-term ageing of this material during mixing and compaction of the mixture on site need to be investigated. A detailed analysis of the costing of the nano charcoal to be used in asphalt pavements will be implemented as well. Finally, this study has shown that NCA has great potential to be utilised in asphalt binders.

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