Jurnal Kejuruteraan 35(3) 2023: 675-681
https://doi.org/10.17576/jkukm-2023-35(3)-15

Microstructural and Thermal Analysis of Warm-Modified Bitumen with Palm Oil Boiler Ash

Norliza Mohd Akhir[a], Shuhaida Harun[b], Naeem Aziz Memon[c], Abdalrhman Milad[d], Muhammad Imran Khan[e], Muhamad Nazri Borhan[a] & Nur Izzi Md Yusoff[a*]

[a]Department of Civil Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Selangor, Malaysia
[b]Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Selangor, Malaysia
[c]Department of Civil Engineering, Mehran University of Engineering & Technology, Indus Hwy, Jamshoro, Sindh 76062, Pakistan
[d]College of Engineering and Architecture, University of Nizwa, P.O. 33 Postal Code 616, Sultanate of Oman
[e]Department of Transportation and Geotechnical Engineering, Risalpur Campus, National University of Sciences & Technology, Islamabad 44000, Pakistan

**Corresponding authors: izzi@ukm.edu.my; P100115@siswa.ukm.edu.my*

Received 5 August 2022, Received in revised form 2 November 2022
Accepted 3 December 2022, Available online 30 May 2023

ABSTRACT

This paper presents the results of an investigation to evaluate the effect of Palm Oil Boiler Ash (POBA) and a chemical warm mix additive, Rediset on the physicochemical and thermal properties of bituminous binders. Modified binder preparation was carried out by varying the composition of POBA (0, 3, 5, 7, and 9%) and Rediset with 2% by total weight of the binder, into a 60/70 penetration grade of bitumen through a wet mixing method. The physicochemical properties of the POBA/Rediset modified binders were examined using Fourier Transform InfraRed (FTIR), while the thermal analysis was conducted using Differential Scanning Calorimetry (DSC), and Thermogravimetry analysis (TGA) techniques. Based on FTIR analysis, POBA/Rediset modified binders have almost similar functional groups as for the control sample (0%) which indicate the compatibility of POBA in the bituminous binder. Meanwhile, the thermos-grams shows an insignificant effect of POBA on the thermal stability of the binder. Overall, the inclusion of POBA as bitumen modifier in warm mix asphalt (WMA) for pavement construction is a promising and potential alternative in lowering the asphalt production temperature without compromising the binder properties.

Keywords: Bitumen; Palm oil boiler ash; Microstructural characterization; Thermal properties; Rediset.

INTRODUCTION

Numerous investigations have been done over time to look into the utilization of local agro-industrial waste material to modify the bitumen. Bitumen modification is an alternative way to produce equivalent pavement performance in order to deal with an excessive amount of traffic and changes in the environment. This exploitation has increased industry awareness to channel their by-product materials toward recycling by other sectors thus produce a cleaner and sustainable industrial environment. Palm oil is a major export commodity in Malaysia which not only produces valuable palm oil, but also produces a large number of biomass products (Kushairi et al. 2019). POBA also called as empty fruit bunch (EFB) ash is derived from dry biomass (shell), mesocarp fibres and unburned kernel shell which have been burned at a temperature of 500-700°C in a boiler furnace for electricity generation and palm oil extraction (Bukit et al. 2018; Ho et al. 2012). The burned palm oil shell and fibres produce a blackish hard crust caused by incineration at high temperatures with a high carbon content of 70-85%. There have been studies that demonstrated POBA also has high silica content roughly 40-86% (Lau et al. 2019; Zarina et al. 2015). The composition difference is influenced by the temperature of the combustion and the vicinity of the source material. The excess supply of POBA as solid waste was being dumped at the plant's disposal site and thus adversely affecting the environment.

Warm Mix Asphalt (WMA) refers as a technology of asphalt mixtures which practically designed to lower the mixing and production temperatures about 25°C to 55°C than the typical Hot Mix Asphalt (HMA) for the purpose of energy saving and less emissions of greenhouse gas (GHG), without affecting the durability, workability and performance characteristics of asphalt pavements (Habal & Singh, 2019; Sukhija & Saboo, 2021; Zhang et al. 2017). Rediset is a chemical warm mix additive which provides active adhesion allowing to coat aggregates that are not completely dry, able to avoids stripping and increases resistance to moisture. This additive is well-known to improve characteristics performance especially tensile strength (Leng et al. 2014), anti-rutting properties, resistance to moisture damage (Varamini 2016), stability (Vahora & Mishra 2017), and fatigue life-span (Abd Duraid 2017). Recently, several studies have attempted using POBA as a possible supplementary material particularly in concrete (Karim et al. 2017; Kueaket & Tonnayopas, 2021; Syafwandi & Fatoni, 2020; Vasudevan, 2016), polymer composite (Ginting et al. 2020; Maghfirah et al. 2018; Rizal et al. 2020; Yahya et al. 2013), also as an efficient low-cost absorbent for pollutants (Aziz et al. 2015); absorbent for dyes dispersed in water solution (Al-Mulali et al. 2015), as well as soil fertilizers (Alfian et al. 2015; Lada & Pombos, 2019; Nelvia, 2017; Ramadhani et al. 2015).

The aim of this research was to comply with sustainable development, which served as its purpose. Limited research has been done on the effects of POBA incorporating Rediset on the physicochemical and thermal characteristics of bituminous binder. Therefore, this study was done to investigate the influence of the modifier; POBA and the warm mix additive; Rediset on of the asphalt binder's modification properties and mechanism. To investigate the microstructure and modification mechanism of POBA modified binder, Fourier Transform Infrared (FTIR) was used to observe the changes in the internal structures and the functional groups of asphalt binder. In addition, the analysis of thermal behaviour was also conducted using Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC).

MATERIAL AND METHODS

MATERIALS AND SAMPLE PREPARATIONS

Base bitumen of 60/70 penetration grade most commonly used in Malaysia and was chosen as a control binder for this research. The bitumen was provided by Sunway Quarry Industries Sdn. Bhd. located in Semenyih, Malaysia. The physicochemical properties of the base binder were measured to assure they complied with the stipulated Malaysian standards, and the results are described in Table 1.

A modifier, palm oil boiler ash (POBA) was supplied by Sedenak Palm Oil Mill in Johor, Malaysia. When POBA is withdrawn from the furnace, it is discovered in blackish sticky lumps of irregular shapes with a size varying from 75µm to 4.75mm. The fresh raw POBA as presented in Figure 1(a), contains 46-47% of moisture. After it has been oven-dried, POBA became whitish grey and porous (as illustrated in Figure 1(b)). According to ASTM C70-20, POBA was heated at a temperature of 70°C for 20 hours to remove moisture before being ground to a finer particle size. In order to remove any potential contaminants, this fine-dried sample was subsequently sieved through no.100 sieve mesh, as shown in Figure 1(c).

Rediset, a warm mix chemical additive (as may be seen in Figure 2), was obtained from Nouryn Surface Chemistry AB, Sweden and is intended to facilitate the production of bituminous mixes at lower temperatures while maintaining good workability. The POBA was added to binder at varying percentages of 3%, 5%, 7% and 9% by total weight of the base binder. Meanwhile, the Rediset was added at the optimum dosage rate of 2% as recommended by the scientific literature (Cheraghian et al. 2020; Habal & Singh 2019; Kataware & Singh 2017; Sengoz et al. 2017). In the study, the base binder was melted beforehand at 170°C. The POBA was further blended to the base binder at a constant speed of 5000rpm for 2hours using a Silverson high-shear mixer until they attained homogeneity mixture. Following the blending of base binder-POBA, Rediset was added to the mixture and blended again for 15 minutes to obtain modified binder.

TABLE 1. PEN 60/70 bitumen physical properties

Properties	Unit	Value	Specification	Standard Test
Penetration (25°C, 100g, 5s)	0.1mm	67	60-70	ASTM D5
Softening point	°C	48.2	min 47	ASTM D36
Ductility (25°C, 5cm/min)	cm	> 150	min 100	ASTM D113
Viscosity (135°C)	mPa.s	777	-	AASTO T316

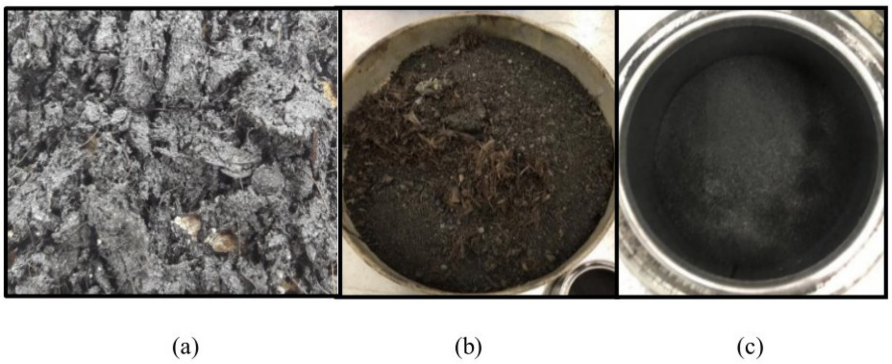

FIGURE 1. (a) Big lumps of POBA (b) oven-dried raw POBA (c) oven-dried sieved POBA

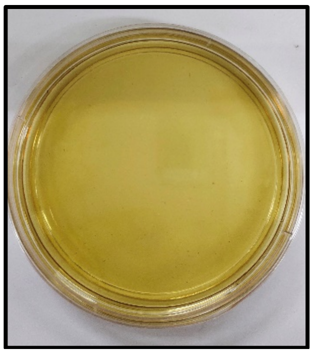

FIGURE 2. Warm mix additive, Rediset

TESTING PROCEDURES

FTIR spectroscopy was used to observe the changes in the internal structures and the functional groups of asphalt binder. A spectrophotometer Nicolet-6700 (Nicolet Instrument Technologies, USA) was used to evaluate the functional properties of all modified binder at 400 to 4000 cm^{-1} wavelengths. In addition, the analysis of thermal behaviour was also conducted using TGA and DSC. TGA in this study was performed using NETZSCH STA449F3 equipment in a nitrogenic atmosphere, at the heating rate of 10 Kelvin/min, in an 85μL alumina crucible. Any modifications to the decomposition curves brought on by the addition of POBA and Rediset to the bitumen were observed. About 9.5mg of binder sample was inserted in an aluminium cell and heated from room temperature to a maximum of 600°C. A microbalance was used to record the change in mass, which was then expressed as a percentage. DSC is a technique that enables the identification of material-related physical changes made by heat exchange. For bitumen, physical changes including the glass transition temperature (T_g) and phase transitions; melting and crystallisation, are crucial.

RESULT AND DISCUSSION

MICROSTRUCTURAL CHARACTERISTICS

The microstructural characterization analysis was performed to evaluate the effects of POBA on the physicochemical properties of the binder modification using FTIR tests. FTIR analysis evaluates the sample's infrared light transmittance level at each wavelength to ascertain the molecular structure and composition of the material. FTIR transmission spectrum of the main functional group of the samples were displayed in Figure 3. In general, each sample has a remarkably similar spectrum with the consistent intensity in each spectrum converging at almost the same point. A number of strong bands; 2920, 2850, 1450 and 1380 cm^{-1} correspond to the C-H stretching in -CH_2- and -CH_3- structures. The two sharp transmittances at 2920 and 2850 cm^{-1}, in particular, can be attributed to the -CH_2- and -CH_3- substituents on aromatic rings, whilst the remaining peaks at 1450 and 1380 cm^{-1} represent C-H bending in -CH_2- and C-H bending in –CH_3-, respectively. The weak absorption peaks created at 1590 and 1650 cm^{-1} is characteristic of C=C stretching vibrations which are related to aromatic compounds. The fingerprint region is described by wave numbers below 1500 cm^{-1}. It may be inferred that the POBA-Rediset and asphalt binder did not interact chemically because there has been no appreciable change in peak position or the appearance of any new peaks at the functional group portion.

THERMAL PROPERTIES ANALYSIS

The thermal properties of modified binder using TGA and DSC techniques was done simultaneously in a single instrument called Simultaneous Thermal Analyzer (STA). The TGA curves showed a single step of degradation, as shown in Figure 4. The thermogram revealed that the curve contains three horizontal zones. As the first zone reflects the removal of moisture and light volatiles or the drying phase, while the second part exhibits continuous mass loss at a cumulative rate proposing thermal degradation of asphalt binder components. The mass loss on the curve continues at a decreasing rate in the third portion, showing evidence of a sublimation process. In order to estimate the temperature at which this rate reaches its maximum, the DTG curve provides information on the rate of change of mass loss with temperature on another curve. The region of the TGA curve with little mass loss corresponds to the first area in the DTG curve where the mass loss rate is almost zero. In the thermal decomposition region, the mass loss increases until it reaches a temperature where the rate of mass loss is maximal.

Without POBA, the base binder started to lose mass at a small rate (2% for both curves TGA and DTG) in 280°C. The highest percentage of mass loss for the DTG curve was around 446.6°C, while the maximum rate of thermal degradation for the TGA curve generally takes place between 470°C and 480°C. The first region of the 3% sample starts at 260°C, climbs to 5% at 270°C, 7% at 280°C, and 9% at 290°C as the proportion of the POBA is added. While all of the tested binder's decomposition temperatures ranged from 452.2°C to 452.9°C. It was demonstrated that all of the POBA samples lost the most weight when the temperature reached >450°C, with the degradation process beginning at >260°C and ending at 500°C. Beyond this point, the decomposition rate starts to decline until it almost reaches zero at 540°C, at which point there is no obvious mass loss. The 0% sample had the largest percentage of weight lost during the process 84.6% while the 5% had the lowest 77.6%. As summary, although basic binder was added with POBA and Rediset, the modified binder remained stable beyond its mixing and compaction temperature, according to the TGA and DTG curves.

To further comprehend the thermal transitions, a DSC test was performed. The DSC thermogram allows for the observation of the physicochemical transitions of glass transition (T_g), melting point (T_m), crystallization (T_c), and oxidation phase (T_{ox}). The temperature of T_g, commonly referred to as the "brittle point," which marks the shift from liquid form into a solid, is always lower than that of T_m. T_g is one of the first thermodynamic parameters to change. T_m is the substance's melting point, or the temperature at which a substance transforms from a solid to a liquid. Additionally, T_{ox} is the temperature at which corrosion at high temperatures is produced by a chemical process involving metallic materials and ambient oxygen (Young, 2016). Figure 5 illustrates how the DSC curves of all MB samples represent a single physicochemical process phase. A modest glass transition was observed by the control sample (0%) at 302.6°C, 3% at 100.3°C, 5% at 263°C, 7% at 76.1°C, and 9% at 134.8°C, followed by the second zone of the glass transition area. Using the Netzsch Proteus Analysis Software, the T_g values and the peak values were calculated. The T_g values were derived from the step function's inflection point. The 7% sample demonstrated greater resistance to low-temperature cracking because lower T_g values are indicative of improved low-temperature performances (Ling et al. 2019). All binders showed the same exothermic peak of T_g at 35°C which were known as wax crystallization. According to the thermograms, all of the examined samples have melting points (T_m) above 400°C, with the exception of 3% and 7% POBA, whose melting points, respectively, were 389.4 and 103°C, respectively, higher than the original crystallisation temperatures. The samples' T_c and T_{ox} levels are undetectable within the tested temperature ranges. In conclusion, it can be shown that, when compared to the DSC curve of the control sample, the addition of POBA and Rediset to the base binder did not significantly alter the physicochemical transitions in terms of thermal characteristics.

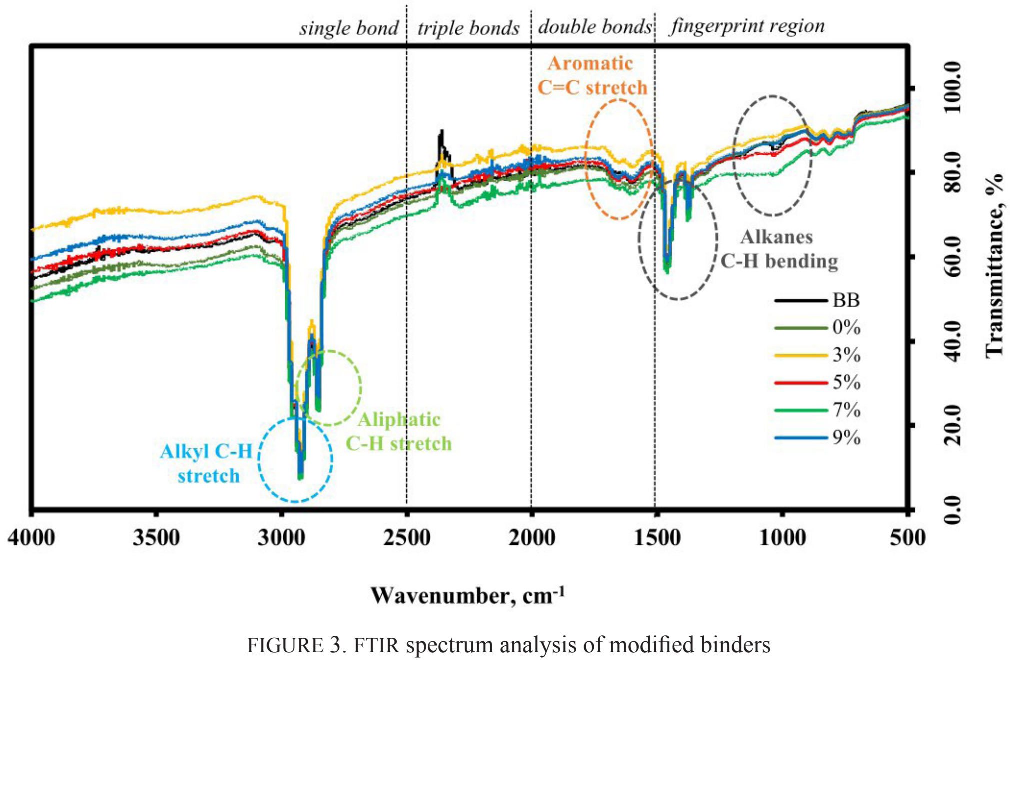

FIGURE 3. FTIR spectrum analysis of modified binders

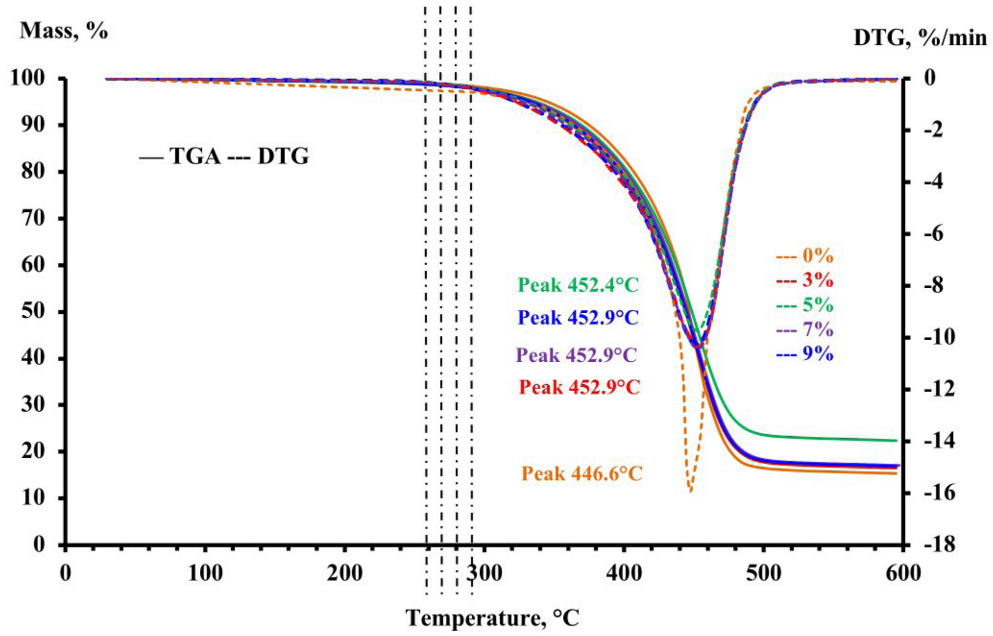

FIGURE 4. Thermogravimetric curves of all POBA modified binder

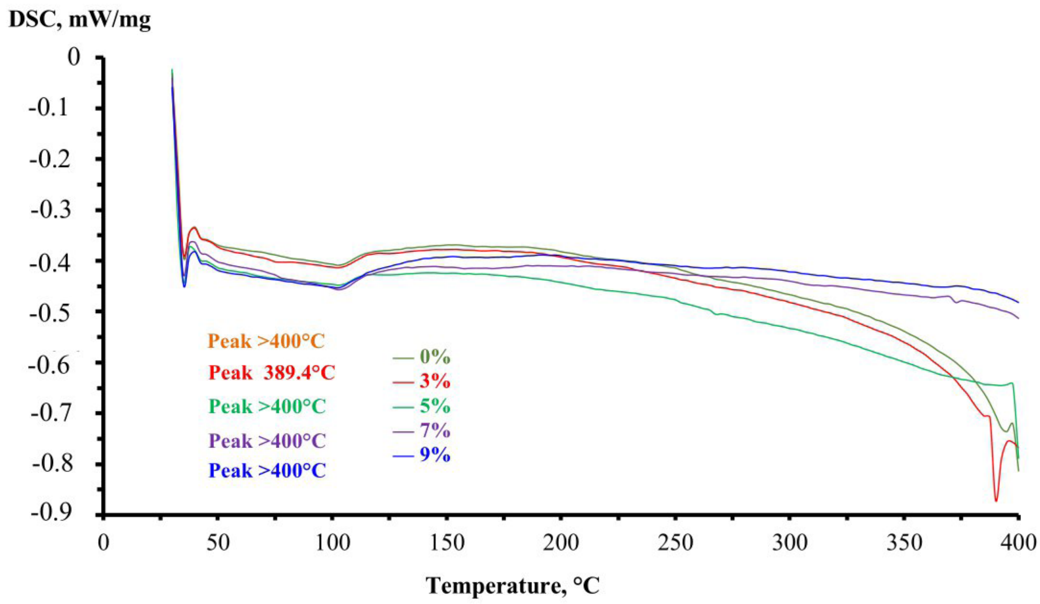

FIGURE 5. The DSC graph of all POBA modified samples

CONCLUSION

The goal of this study is to investigate the impacts of POBA on the microstructural properties and thermal behaviour of asphalt binder incorporating with Rediset. According to FTIR analysis, there was no chemical interaction or any significant shift in the peak at the functional groups; therefore, POBA/Rediset modified binders have almost similar functional groups as the control sample (0%), indicating POBA compatibility in the asphalt binder. Meanwhile, the DSC results showed similar trends for the tested bitumen, with 7% POBA sample having the lowest T_g and T_m value. However, the TGA performed on all samples revealed that the degradation process occurred at temperatures >300°C >450°C. Overall, all the thermosgrams shows an insignificant effect of POBA on the thermal stability of the binder. In conclusion, the inclusion of POBA as bitumen modifier in WMA binder for pavement construction is a promising and potential alternative in lowering the asphalt production temperature without compromising the binder properties.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Ministry of Higher Education, Malaysia (MOHE) that has funded this research grant through FRGS/1/2020/TK02/UKM/02/2.

DECLARATION OF COMPETING INTEREST

None

REFERENCES

Abd Duraid, M. 2017. Characterisation of warm asphalt mixtures with addition of reclaimed asphalt pavement materials (University of Liverpool). https://livrepository.liverpool.ac.uk/3006981/

Al-Mulali, M. Z., Awang, H., Abdul Khalil, H. P. S., & Aljoumaily, Z. S. 2015. The incorporation of oil palm ash in concrete as a means of recycling: A review. *Cement and Concrete Composites* 55: 129–138.

Alfian, D. F., Nelvia, & Yetti, H. 2015. Pengaruh pemberian pupuk kalium dan campuran kompos tandan kosong kelapa sawit dengan abu boiler terhadap pertumbuhan dan hasil tanaman bawang merah (Allium asacalonicum L.). *Jurnal Agroteknologi* 5(2): 1–6.

Aziz, A. S. A., Manaf, L. A., Man, H. C., & Kumar, N. S. 2015. Equilibrium studies and dynamic behavior of cadmium adsorption by palm oil boiler mill fly ash (POFA) as a natural low-cost adsorbent. *Desalination and Water Treatment* 54(7): 1956–1968.

Bukit, N., Ginting, E. M., Pardede, I. S., Frida, E., & Bukit, B. F. 2018. Mechanical properties of composite thermoplastic hdpe / natural rubber and palm oil boiler ash as a filler. *The 8th International Conference on Theoretical and Applied Physics* 1120(2018): 1–8.

Cheraghian, G., Cannone Falchetto, A., You, Z., Chen, S., Kim, Y. S., Westerhoff, J., … Wistuba, M. P. 2020. Warm mix asphalt technology: An up to date review. *Journal of Cleaner Production* 268: 122128.

Ginting, E. M., Bukit, N., Frida, E., & Bukit, B. F. 2020. Microstructure and thermal properties of natural rubber compound with palm oil boilers ash for nanoparticle filler. *Case Studies in Thermal Engineering* 17: 100575.

Habal, A., & Singh, D. 2019. Effects of warm mix asphalt additives on bonding potential and failure pattern of asphalt-aggregate systems using strength and energy parameters. *International Journal of Pavement Engineering* 22(4): 467–479.

Ho, W. W. S., Ng, H. K., & Gan, S. 2012. Development and characterisation of novel heterogeneous palm oil mill boiler ash-based catalysts for biodiesel production. *Bioresource Technology* 125: 158–164.

Karim, M. R., Hashim, H., Abdul Razak, H., & Yusoff, S. 2017. Characterization of palm oil clinker powder for utilization in cement-based applications. *Construction and Building Materials* 135: 21–29.

Kataware, A. V., & Singh, D. 2017. Evaluating effectiveness of WMA additives for SBS modified binder based on viscosity, Superpave PG, rutting and fatigue performance. *Construction and Building Materials* 146: 436–444.

Kueaket, K., & Tonnayopas, D. 2021. Compressive strength and durability performance of mortar containing palm oil boiler clinker aggregate, rice husk ash, and calcium bentonite. *Journal of Applied Engineering Science* 19(1): 193–203.

Kushairi, A., Ong-Abdullah, M., Nambiappan, B., Hishamuddin, E., Bidin, M. N. I. Z., Ghazali, R., Parveez, G. K. A. 2019. Oil palm economic performance in Malaysia and R&D progress in 2018. *Journal of Oil Palm Research* 31(2): 165–194.

Lada, Y. G., & Pombos, N. S. 2019. Studi pemanfaatan pupuk abu boiler pada pertumbuhan bibit tanaman kakao (Theobroma cacao L.). *Jurnal Agercolere* 1(1): 25–29.

Lau, S. Y., Phuan, S. L., Danquah, M. K., & Acquah, C. 2019. Sustainable palm oil refining using pelletized and surface-modified oil palm boiler ash (OPBA) biosorbent. *Journal of Cleaner Production* 230: 527–535.

Leng, Z., Gamez, A., & Al-Qadi, I. L. 2014. Mechanical property characterization of warm-mix asphalt prepared with chemical additives. *Journal of Materials in Civil Engineering* 26(2): 304–311.

Ling, T., Lu, Y., Zhang, Z., Li, C., & Oeser, M. 2019. Value-added application of waste rubber and waste plastic in asphalt binder as a multifunctional additive. *Materials* 12(1280): 1–17.

Maghfirah, A., Dharma Sembiring, A., & Iskandar, M. 2018. Preparation and characterization of polymer composite tile based on boiler ash waste from palm oil industry and fiber from waste tire reinforced by asphalt. *FISITEK : Jurnal Ilmu Fisika Dan Teknologi* 2(1): 8–14.

Nelvia, Y. H. 2017. Pengaruh pemberian abu boiler terhadap pertumbuhan dan hasil bawang merah (Allium ascalonicum L .) di lahan gambut. *Jurnal Dinamika Pertanian* XXXIII 21–27.

Ramadhani, F., Aryanti, E., & Saragih, R. 2015. Pemanfaatan beberapa jenis dan dosis limbah kelapa sawit (Elaeis guinensis Jacq) terhadap perubahan pH, N, P, K tanah podsolik merah kuning (PMK). *Jurnal Agroteknologi* 6(1): 9–16.

Rizal, S., Fizree, H. M., Hossain, M. S., Ikramullah, Gopakumar, D. A., Wan Ni, E. C., & Abdul Khalil, H. P. S. 2020. The role of silica-containing agro-industrial waste as reinforcement on physicochemical and thermal properties of polymer composites. *Heliyon* 6(3): e03550.

Sengoz, B., Topal, A., Oner, J., Yilmaz, M., Dokandari, P. A., & Kok, B. V. 2017. Performance evaluation of warm mix asphalt mixtures with recycled asphalt pavement. *Periodica Polytechnica Civil Engineering* 61(1): 117–127.

Sukhija, M., & Saboo, N. 2021. A comprehensive review of warm mix asphalt mixtures-laboratory to field. *Construction and Building Materials* 274*:* 121781.

Syafwandi, & Fatoni, A. 2020. Effect of use of substituted oil palm shell boiler ash on cement and substituted glass powder on fine aggregate on concrete compressive strength. *Journal of World Conference (JWC)* 2(2): 92–98.

Vahora, S. I., & Mishra, C. B. 2017. Investigating the Performance of Warm Mix Additives. *International Journal of Current Engineering and Technology* 7(3): 1011–1015.

Varamini, S. 2016. Technical, Economic and Environmental Evaluation of Warm Mix Asphalt and Coloured Asphalt for Usage in Canada. *Ph.D. Thesis, University of Waterloo, Waterloo, ON, Canada*.

Vasudevan, G. 2016. Performance using boiler ash clinkers as replacement for course aggregates in concrete. *Materials Science Forum*: 83–88.

Yahya, Z., Abdullah, M. M. A. B., Hussin, K., Ismail, K. N., Sandu, A. V., Vizureanu, P., & Razak, R. A. 2013. Chemical and physical characterization of boiler ash from palm oil industry waste for geopolymer composite. *Revista de Chimie*.

Young, D. J. 2016. *High Temperature Oxidation and Corrosion of Metals*. 2nd edition. In S. Watson (Ed.), *Elsevier Publications* (Second). New South Wales, Sydney: John Fedor.

Zarina, Y., Al Bakri, A. M. M., Kamarudin, H., Khairul Nizar, I., & Razak, A. R. 2015. Effect of NaOH concentration on microstructure of boiler ash based geopolymer. *Materials Science Forum*: 173–178.

Zhang, J., Airey, G. D., Grenfell, J., & Yao, Z. 2017. Laboratory evaluation of Rediset modified bitumen based on rheology and adhesion properties. *Construction and Building Materials* 152: 683–692.