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THE USE OF LDPE PYROLYSIS RESIDUE AND PALM OIL BOILER CRUST ASH AS ADDITIVES FOR ASPHALT BINDER

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ABSTRACT

This research utilizes LDPE plastic pyrolysis residue and boiler crust ash as additives in asphalt modification to improve the hydrophobic properties of asphalt. Tests were conducted with time variations of 15, 30, 45, 60, and 75 mins. Contact angle measurements of asphalt mixtures, with the addition of LDPE plastic pyrolysis residues and boiler scale ash, as well as asphalt mixtures with the addition of LDPE plastic pyrolysis residues and silica, resulted in contact angle values greater than 90°, indicating that the asphalt mixtures possess hydrophobic properties. Characterization results using FTIR analysis showed the presence of C-H, O-H, Si-O-Si, and Si-O functional groups in the modified asphalt samples. The modification of asphalt with these additives can enhance its hydrophobic properties.

Keywords: Asphalt Binder; Hydrophobic; LDPE, Pyrolysis Residue; Additives.

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INTRODUCTION

Highways are very important transportation infrastructure in everyday life. Currently, highways serve as traffic connecting lines from one place to another. The movement of human activities on the highway affects the asphalt paving.[1] Good highway asphalt paving, which has high stability, will positively impact traffic smoothness. The production of highway asphalt paving depends on the materials used, the composition of the material mixture, and the processing of these materials. Waste materials from industrial management can be utilized as additives to improve the characteristics of highway paving.[2] Based on the climate and temperature conditions in Indonesia, the asphalt used has a penetration value of 60/80. Asphalt with a penetration of 60/80 is less flexible and less stable in its properties, so it requires additives to enhance its characteristics. Water can dissolve components in the asphalt mixture used for road paving, which reduces the quality of the asphalt mixture. The decrease in asphalt content leads to reveling (grain release) and stripping (surface peeling). One of the efforts to reduce water absorption in asphalt is to improve its performance from hydrophobic to super-hydrophobic. Hydrophobicity is determined by the contact angle of water with the surface. The contact angle (θ) is defined by the line of intersection between the liquid contact line and the line from the bottom of the liquid droplet. A hydrophobic layer has a contact angle value greater than 90°, while a super-hydrophobic layer has a contact angle value greater than 150°.[3] To reduce the level of water absorption in asphalt, additional substances are needed. In this study, the additives used for asphalt modification are a mixture of LDPE (Low-Density Polyethylene) plastic pyrolysis residues with palm oil boiler crust ash and silica (SiO_2) extracted from palm oil boiler crust ash. Plastic waste that is difficult to decompose has a negative impact on the surrounding environment; therefore, effective management is essential. One of the efforts made is the use of the pyrolysis method, which is based on the principle of decomposing material without oxygen. The pyrolysis process of plastic waste produces a residue with a high carbon content. Generally, this pyrolysis residue is used for compost or fertilizer. Therefore, further management is needed for the utilization of plastic waste pyrolysis residue. The plastic waste used in this research is LDPE plastic, and the use of LDPE plastic waste residues aims to increase asphalt stability while reducing LDPE plastic

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waste. Palm kernel ash is obtained from crushed palm fruit fibres and shells burned in a furnace at temperatures of 500°C to 700 °C.[4] The silica (SiO_2) content in palm kernel ash plays a role in increasing compressive strength, thereby minimizing shrinkage and cracking in asphalt. The utilization of silica to enhance hydrophobic properties is based on its characteristics. According to Susanti *et al.* (2020),[5] modifying asphalt with silica can increase shear strength and maintain asphalt resistance at high temperatures. The increase in temperature affects the shear modulus, leading to a decrease in modulus. In this study, silica extract was obtained from palm oil boiler crust ash using a leaching method with an acid solvent. based on research conducted by Dalhat and Adenia (2020),[6] LDPE can improve the hydrophobic properties of asphalt. Mixing asphalt with LDPE produces a contact angle that meets the criteria for a superhydrophobic contact angle, with time variations of 15-, 30-, and 45-min yielding values of 158°, 157°, and 156°, respectively. Research by Abdurahman *et al.* (2019),[7] also utilized boiler crust ash as an additive in asphalt modification, resulting in an 80% increase in ductility and an increase in asphalt contact angle from 91° to 110°. This literature review serves as the basis for this research. To improve the hydrophobic properties of asphalt and enhance its performance, continuous research is being conducted by observing the mixture of plastic additives from pyrolysis.

EXPERIMENTAL

Material and Methods

The materials used were Performance Grade (PG) 60-70 asphalt obtained from PT Guna mulya, Jakarta. LDPE plastic waste pyrolysis residue obtained from the Faculty of Science and Technology, palm oil boiler crust ash, NaOH, HCl, and distilled water.

LDPE Plastic Pyrolysis Residue

The LDPE plastic that has been prepared is cut into small pieces. Then, the LDPE plastic was put into the pyrolysis tube. The pyrolysis process is carried out by heating at a temperature of 150 ºC for 2 h. Then, the formed residue was separated and cooled down. The residue formed was crushed until fine and mixed with a binder in the form of asphalt.

Extraction of SiO_2 from Palm Oil Boiler Crust Ash

Oil palm boiler crust ash was refurnished at 750 ºC for 6 h. Then, the boiler crust ash was sieved using a sieve. 12 g of boiler crust ash was added with 150 mL of 1 M NaOH solution then stirred and refluxed for 4 h at 90 ºC. The results obtained were cooled and filtered to separate the filtrate and residue. The resulting filtrate was then added HCl drop by drop until a pH of 9 was formed. The solution was allowed to stand for 2 x 24 h to form a gel. The gel was neutralized and filtered with filter paper. The resulting residue was dried using an oven at 120 ºC. Then the solids were crushed to form fine granules. Then proceed with characterization using X-ray fluorescence (XRF).

Asphalt Modification with LDPE Plastic Pyrolysis Residue and Palm Oil Boiler Crust Ash

Performance Grade (PG) 60-70 asphalt was melted in an oven at 165 ºC for 35 to 45 min as much as 95% of the total weight of the mixture. Then, LDPE plastic pyrolysis residue and palm oil boiler crust ash were added as much as 5% of the total weight of the mixture. Then, stir with a stirrer for 1 h. The liquid asphalt mixture was stirred and poured into a mold with an aluminum base measuring 30 x 20 x 4 mm. Then, the asphalt mixture layered with LDPE plastic pyrolysis residue and boiler crust ash, was baked in an oven at 100 ºC. The baking temperature used was not too high to avoid excessive melting of the asphalt substrate (15, 30, 45, 60, and 75) min. All samples were tested within 24 hours after drying. The modified asphalt samples were characterized by FT-IR (Fourier Transform Infrared).

Asphalt Modification with LDPE Plastic Pyrolysis Residue and SiO_2 Extract from Palm Oil Boiler Crust Ash

Modified asphalt of Performance Grade (PG) 60-70 was melted in an oven at 165 ºC for 35 to 45 mins for 95% of the total weight of the mixture. Then, added LDPE plastic pyrolysis residue and SiO_2 extract from palm oil boiler crust ash each as much as 5% of the total weight of the mixture. Then, stir with a stirrer for 1 h. The liquid asphalt mixture was stirred and poured into a silicone mold with an aluminum base measuring 30 x 20 x 4 mm. Then, the asphalt mixture coated with LDPE plastic pyrolysis residue was placed in an oven at 100 ºC. The curing temperature used was not too high to avoid excessive melting of

the asphalt substrate (15, 30, 45, 60, and 75) min. All samples were tested within 24 hours after drying. The modified asphalt samples were characterized by FT-IR (Fourier Transform Infrared).

Characterization of Asphalt Modification

A water contact angle measurement test was conducted using a contact angle system. The WCA test was conducted using de-ionized water droplets, at room temperature and humidity of 23 ± 1.50C and 50-60%, respectively. The contact angle was determined by repeating three times at three different surface locations, then recorded and reported. FTIR testing was carried out as a characterization to determine the functional groups and interfacial interactions of LDPE plastic pyrolysis residue, boiler crust ash, and Silica (SiO_2) with asphalt binder.

RESULTS AND DISCUSSION

Preparation of Boiler Scale Ash

The boiler scale ash was calcined using a furnace at 750˚C for 6 h to remove impurities contained in the boiler scale ash. Calcination carried out at temperatures >700˚C will produce amorphous silica. Based on Joharudi *et al.,* (2019),[8] amorphous silica has the potential to improve the characteristics of material because silica in amorphous form is easier to undergo destruction. Before calcination, boiler crust ash is black, indicating a high carbon content. After calcination, the ash changed color to grey. The color change that occurs indicates a decrease in the carbon content contained in the boiler crust ash. Boiler crust ash before and after the furnace is shown in Fig.-1. According to Varun Kumar research (2024),[9] in the calcination process, there is a decomposition of CO_2 compounds with H_2O and leaves silica compounds (SiO_2). The reaction formed in the calcination process can be found in Eq.-1.

$$(\text{Compounds C, H and Si})_{aq} + 3O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} + SiO_{2(s)} \quad (1)$$

Fig.-1: Boiler Scale Ash and Boiler Scale Ash after Furnace

Extraction of Silica from Boiler Crust Ash

The method used in the silica extraction process is the alkali method. According to Ardaniswari *et al.* (2020),[10] the alkaline method is based on the formation of a sol-gel, influenced by the high solubility of silica in alkaline solutions. In the research conducted, the silica extraction method used refers to the study by Syafriadi *et al.* (2021), where 12 g of boiler crust ash that had been in the furnace was dissolved in 1M NaOH, then refluxed and stirred using a stirrer at 90 °C for 4 hours. The addition of the NaOH solution aims to bind the silica contained in the boiler crust ash to produce sodium silicate compounds (Na_2SiO_3). The concentration and time used during the research affect the extraction results. Based on the previous research,[12] the silica content produced was influenced by variations in time and NaOH concentration. The higher the concentration of NaOH and the longer the time used, the higher the silica content produced. This is influenced by the interaction that occurs between the extractor and the solute. According to Fadilah *et al.* (2019),[12] in the formation of sodium silicate, the NaOH solution dissociates to form Na^+ and OH^- ions. The Si element is more electropositive and will form less stable [SiO_2OH] intermediates because the electronegativity of O in SiO_2 is quite high. OH^- ions will bind with hydrogen to form water molecules, and Na^+ ions will balance the negative charge of SiO_2 ions to form sodium silicate (Na_2SiO_3). The reaction that occurs in the formation of sodium silicate can be seen in Eq.-2.

$$SiO_{2(s)} + NaOH_{(aq)} \rightarrow Na_2SiO_{3(aq)} + H_2O_{(l)} \quad (2)$$

After refluxing, the results obtained will be filtered. Filtering is done to separate the residue from the filtrate containing sodium silicate. In the next process, the acidification of sodium silicate is carried out by adding a 32% hydrochloric acid (HCl) solution. The HCl solution is used as an acid because it can produce greater porosity compared to other acidic compounds. The addition of the HCl solution continues until the pH reaches 9; this is because silica has low solubility at a pH of less than 10, specifically between 7 and 9. According to Meidinariasty *et al.* (2020),[14] the concentration of hydrochloric acid used affects the yield of silica obtained. The higher the concentration of hydrochloric acid, the higher the yield of silica produced. The reaction can be seen in Reaction Eq.-3.

$$Na_2SiO_{3(aq)} + 2HCl_{(aq)} \rightarrow SiO_{2(s)} + H_2O_{(g)} + 2NaCl_{(aq)} \quad (3)$$

The hydrogel formed during the acidification and dwell process will be washed until the pH is neutral and then placed in an oven at 110°C. The resulting hydrogel is washed with distilled water to remove Na^+ ions, metal oxides, and excess acid. Drying at 110°C aims to reduce the water content until it is dehydrated and forms silica gel ($SiO_2 \cdot xH_2O$). The silica gel that has been baked will be crushed to produce silica with a small particle size and a white color. The silica produced through the extraction process from boiler crust ash was tested using XRF analysis. The results of the XRF analysis can be seen in Table-1.

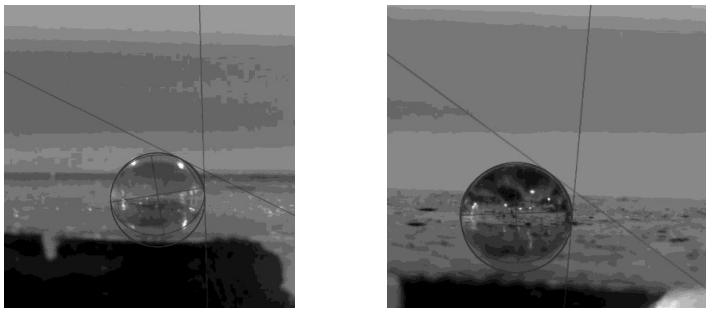
Table-1: XRF results before and after extraction from palm oil boiler crust ash

Compounds (%)	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	V_2O_5	MnO	Fe_2O_3
Before	38.00	9.00	2.50	13.60	29.90	0.39	0.01	0.38	5.59
After	96.100	-	-	2.680	0.820	-	-	0.023	0.190

Based on Table-1, there is an increase in the level of silica (SiO_2) found in boiler crust ash. Unextracted boiler crust ash has a silica (SiO_2) content of 38% and after extraction, the silica content is 96.1%. Based on the data obtained, it is known that the silica extraction process using the sol-gel method can increase the purity of silica compounds contained in boiler crust ash. So this method can be used as a reference for increasing silica levels in the extraction process.

Water Contact Angle Testing

Fig-2 shows the contact angle of (a) modified bitumen with LDPE plastic pyrolysis residue and boiler scale ash variation 45 and (b) modified bitumen with LDPE plastic pyrolysis residue and silica 30 min. Contact angle measurement was carried out to determine the amount of contact angle value used to indicate the hydrophobic nature of the sample. Hydrophobic properties are indicated by contact angle values >90˚C. In this study, contact angle measurements were made on asphalt samples before additives were added and the test results are shown in Table-2. Based on tests on asphalt samples without the addition of additives, the average value of the contact angle is 97.75, which shows the contact angle value that fulfills hydrophobic properties. However, the contact angle value produced has not reached the optimum because the contact angle value produced tends to be small. Therefore, additives were added to improve the hydrophobic properties of asphalt.



(a) (b)

Fig.-2: Contact Angle Measurement Results (A) Modified Bitumen with LDPE Plastic Pyrolysis Residue and Boiler Scale Ash Variation 45 (B) Modified Bitumen with LDPE Plastic Pyrolysis Residue And Silica 30 Min.

The modified asphalt mixture containing LDPE plastic pyrolysis by-product, boiler crust ash, and silica showed a contact angle value greater than 90˚C are shown in Table-2. This shows that the modified

asphalt mixtures have hydrophobic characteristics, or the capacity to reject water. The asphalt mixture containing LDPE plastic pyrolysis residue and boiler crust ash had the maximum contact angle value for the 45-minute time variation, measuring 126.340˚. In comparison, the 75-min time variation produced the lowest contact angle value of 113.360˚. The asphalt mixture with LDPE plastic pyrolysis residue and silica had a maximum contact angle value of 114.060˚ after 30 minutes. In comparison, the 75-minute time variation yields the lowest score of 105.310˚. The asphalt alteration samples were analyzed and found to have hydrophobic qualities (>90˚C) but not yet superhydrophobic properties (>150˚C).

Table-2: The Results of Contact Angle from Asphalt and Modified Asphalt

Time variations (min)	Average contact angle		
	Asphalt	A mixture of asphalt, LDPE plastic pyrolysis residue, and boiler scale residue	A mixture of asphalt, LDPE plastic, pyrolysis residue, and silica
-	97.75	-	-
15	-	116.95˚	110.32˚
30	-	121.95˚	114.06˚
45	-	126.34˚	108.47˚
60	-	116.09˚	106.84˚
75	-	113.36˚	105.31˚

FTIR Characterization

A 30-minute fluctuation time for silica and an asphalt mixture containing LDPE plastic pyrolysis residue was analyzed using Fourier transform infrared spectroscopy (FTIR). Fig-3 and Fig-4 display the resulting spectra. According to the research conducted by Jiang *et al.* (2017),[15] the spectra show absorption peaks at 2918.336 and 2848.907 cm^{-1}, indicating stretching vibrations of the C-H group. This information is supported by Fig.-3.

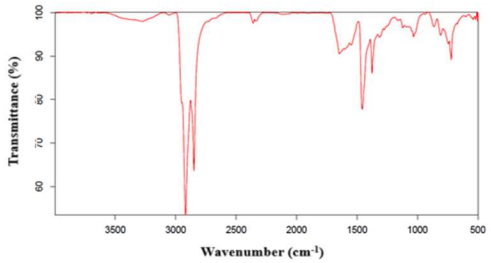


Fig.-3: FTIR Spectrum of Asphalt Mixture with LDPE Plastic Pyrolysis Residue and Silica for 30 Min Time Variation

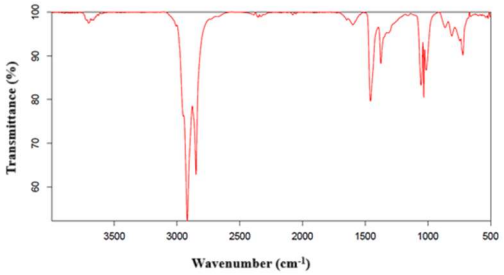


Fig.-4: FTIR Spectra of Modified Bitumen with LDPE Plastic Pyrolysis Residue and Boiler Crust Ash for 45 min Time Variation

Additionally, the absorption peak at a wavenumber of 1457.573 cm^{-1} suggests the presence of stretching vibrations of the C-H groups. Asphalt primarily consists of compounds with C-H stretching vibrations. The vibration of the O-H bending group is indicated by the absorption peak at 1599.101 cm^{-1}. Asphalt contains water molecules, which are represented by the O-H group. Absorption bands at 1054.669, 1032.899, and 1013.981 cm^{-1} suggest the existence of stretching vibrations in the siloxane (Si-O-Si) group. The siloxane (Si-O-Si) groups are further identified by exhibiting absorption peaks at

wavenumbers 809.000, 745.195, and 720.824 cm^{-1}. The presence of siloxy (Si-O) stretching vibrations and bending of siloxy (Si-O) groups is indicated by these wavenumbers, in line with the research of Geetha *et al.* (2016).[16] Interactions between silica and asphalt, as indicated by siloxane groups (Si-O-Si), siloxy threads, and siloxy groups (Si-O), do not lead to a chemical reaction between the two substances. Absorption peaks at 2849.464 and 2918.234 cm^{-1} are shown in the spectra in Fig.-4. The presence of C-H group stretching vibrations, the main constituent groups in asphalt, can be detected at these wavelengths. The absorption peak at wave number 1456.241 cm^{-1} also indicates the presence of C-H group stretching vibrations. Binding vibrations of water molecules' O-H groups are shown by the absorption peaks at 1646.064 and 1548.266 cm^{-1}. In addition, the stretching vibrations of siloxane groups (Si-O-Si) are indicated by the absorption peaks at 1121.911 and 1032.183 cm^{-1}, whereas the stretching and bending vibrations of siloxy groups (Si-O) are indicated at 862.428, 807.741, 744.604, and 720.067 cm^{-1}. Absorption peaks corresponding to C-H, O-H, Si-O-Si, and Si-O functional groups suggest that asphalt and silica interact, but no chemical reaction takes place. Asphalt-modified LDPE plastic pyrolysis residue and silica time variation of 30 mins and asphalt-modified LDPE plastic pyrolysis residue and boiler crust ash time variation of 45 mins both have the same functional group content, according to the spectra. The samples consist of four distinct groups: C-H, O-H, Si-O-Si, and Si-O. This proves that the amount of functional groups in asphalt modification is unaffected by differences in heating duration.

CONCLUSION

The research findings indicate that asphalt can be modified by adding additives such as LDPE plastic pyrolysis residue and boiler crust ash. Variations in time of 15, 30, 45, 60, and 75 mins result in contact angle values above 90˚C, with specific values of 116.950˚, 121.950˚, 126.340˚, 116.090˚, and 113.360˚. This proves that the asphalt alteration has hydrophobic characteristics. Furthermore, the presence of hydrophobic characteristics was further demonstrated by asphalt modification using the same additives and time variations, which resulted in contact angle values above 90˚C, namely 110.320˚, 114.060˚, 108.470˚, 106.840˚, and 105.310˚. A larger cohesive force than an adhesive force is responsible for the formation of hydrophobic characteristics. The functional groups in asphalt modified with LDPE plastic pyrolysis waste and boiler crust ash were comparable to those in asphalt modified with silica, according to the FTIR analysis that characterized the asphalt modification.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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