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ORIGINAL RESEARCH PAPER

Behaviour of Hot Mix Asphalt Incorporating Untreated and Treated Waste Cooking Oil

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Abstract

The recyclability of waste cooking oil (WCO) as rejuvenator for aged asphalt mixture improved the serviceability of pavement itself. Currently, the researcher is exploring the new potential of WCO as modifier for binder modification. However, the issue of compatibility properties in the modification of binder with WCO arises since the poor mechanical performance of asphalt mixture is globally recorded thus reflected the weakness of adhesion bonding inside the pavement material. Basically, the superior mechanical performance of asphaltic concrete exhibited good adhesion bonding between binder-aggregates interaction in bituminous mixture. In fact, the potential of high adhesiveness binding properties is affected by the chemical theory which is mostly related to the polarity factor. Therefore, it is vital to conduct the chemical analysis and microstructure observation to obtain a comprehensive understanding of the polar group behaviour for the internal structure in pavement material that influencing the adhesion performance for the structural arrangement material in the mixture. Therefore, excellent adhesion is capable of improving mechanical performance of Hot Mix Asphalt (HMA). The identification of chemical composition for polarity group determination was identified by using Gas Chromatography-Mass Spectrometry (GC–MS). Meanwhile, the adhesiveness measurement between binder-aggregate interactions in the mixture was observed with Field Emission Scanning Electron Microscope (FESEM) which physically resulting in mechanical performance by conducting resilient modulus test, dynamic creep test and indirect tensile strength (ITS) test. Results showed that the incompatibility characteristic is revealed between untreated WCO and conventional binder (PEN 60/70) based on the identification of polar and non-polar compounds interaction. Thereby, exhibits the existence of gap and void structure arrangement in HMA through FESEM visualization hence affecting the poor mechanical strength of asphalt mixture.

Keywords Waste cooking oil · Polarity · Adhesion · Hot mix asphalt

1 Introduction

The generation of kitchen waste particularly in WCO obtained from frying activities has increased due to the demand of food stuff. However, the common habits of disposing WCO into the kitchen sink have engaged many drawbacks on environmental issues. According to Zahoor et al. [37], the improper way of WCO's disposal has triggered the contamination of water and soil, disrupt the ecosystem of aquatic life and stimulate the wastewater sewage treatment cost for maintenance due to clogging problem. Hence, waste recycling of WCO is viewed as an alternative that can be adapted to cater the pollution matter. Moreover, the good adhesion mechanism between the binder and aggregates particles in bituminous mixture was related with an improvement of mechanical performance for asphalt mixture

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[36]. The adhesion characteristic was affected by the internal microstructure component. Fundamentally, the chemical theory is identified as significant major factors which contributes to the adhesion rate potential. According to Jose et al. [20], the characterisation of the material properties at the smaller length scale influencing the behaviour of bitumen at macroscopic measurement based on the determination from the chemical analysis, in which it can be identified based on the polarity group. Bahia et al. [10] and Moraes et al. [25] stated that the determination of polarity is categorised as the chemical composition of the material that is required to be chemically investigated. This is also supported by Xu et al. [35], in which a comprehensive understanding on the chemistry of binder is important as the physical and mechanical properties of the binder were influenced by the chemical composition possessed in asphalt binder materials. To understand the fundamental mechanism of adhesion properties comprehensively, the polarity group is determined by referring to the presence of chemical composition inside the pavement material that attributed to the high strength of adhesion binding between binder-aggregate in asphalt mixture [26]. The chemical analysis was evaluated by performing Gas Chromatography-Mass Spectrometry (GC–MS) for polarity group identification and microstructure observation through Field Emission Scanning Electron Microscope (FESEM) for adhesion performance investigation. The effectiveness of adhesion binding between binder-aggregate in the mixture is proven by the high strength to resist permanent deformation [1] through resilient modulus test, dynamic creep test, and indirect tensile strength (ITS) test.

Several studies focused on the microstructure observation of waste cooking oil (WCO) in modified binders have been reviewed. An analysis on the existence of chemical composition concerning functional group for modified binder by incorporating biodiesel by-product derived from WCO as a modifier was carried out by Sun et al. [30] by using Fourier Transform Infrared (FTIR). Based on the FTIR observation, the similarity of elemental composition between both materials of control binder and biodiesel by-product was recorded which consisted of saturated hydrocarbon, amides and aromatic compounds. However, a noticeable difference in functional group was identified wherein the control binder contains sulfinyl compounds meanwhile lipid compounds has existed in biodiesel by-product. Basically, lipids can be categorized in fat group, which is non-polar while asphalt binder in nature is identified as polar group. According to Nurdin et al. [27], the chemical standpoint stated that the fat group has high solubility in the same fat source component. It is expected that the incompatibility issue will occur during the substitution of biodiesel by-product derived from waste cooking oil in binder, which in turn contributed to the detrimental effect on the rheological performance, thereby affecting to the poor mechanical performance of asphalt mixture.

The addition of an oil-based source for binder modification shows an improvement in thermal cracking resistance at low temperature as reported by numerous previous researchers. However, the rutting resistance performance showed an adverse effect, in which the deterioration at high-temperature performance was observed with the addition of WCO as a modifier in binder. It is evidenced with the previous findings by Wen et al. [33] and Maharaj et al. [24], which stated that the poor rutting resistance performance at high temperature was recorded when WCO was substituted for asphalt binder modification. Practically, the softening effect is exhibited on the modified binders with WCO and it is expected that the soft binder contributes to poor performance in permanent deformation resistance due to unable to withstand with high-temperature exposure. Despite the minimum addition of WCO in binder, the detrimental effect is noticeable in effecting the modified binders, which in turn reduces adhesive properties to aggregate and thus leads to the poor mechanical performance of asphalt mixture. There is no conclusion that can be drawn and the justification is presently not well documented in explaining the reason for this mechanism. The justification of the main factor that attributed to this issue where it is due to the incompatibility characteristic between the asphalt binder and oil based source, thereby inducing instability problem in the chemical reaction between oil in modified binders and asphalt mixture [12]. This can be depicted that there is a constraint factor that has refused the occurrence molecule interaction in making a strong chemical bonding in the modified binders with WCO. Due to the arising issue, the investigation on the compatibility properties between WCO and asphalt binder becomes a major concern in this study. Therefore, it is significant to perform chemical analysis by conducting GC–MS to discover whether untreated WCO and treated WCO are compatible with the binder for binder modification based on the polarity group determination. Thereby, observing how the compatibility properties effecting to the adhesion performance between binder-aggregates which influencing particle arrangement inside the mixture through FESEM image visualization. Thus, high adhesiveness property is proven based on the superior mechanical performance of HMA.

2 Materials and Experimental Works

2.1 Virgin Binder

In this study, PEN 60/70 asphalt binder was used as control asphalt binder. The binder source was supplied by Eksklusif Alfa Enterprise located in Selangor, Malaysia and met all the requirements specified by the Malaysian Public Works Department standard. The penetration and softening point for binder PEN 60/70 are recorded as 62 dmm and 50 °C which indicates that the physical properties of control binder are acceptable and allowed to be used for control binder as it follow the specification.

2.2 Untreated WCO and Treated WCO

Basically, two types of modifier were added into control binder to produce modified binders which can be divided into untreated WCO and treated WCO. For untreated WCO, this modifier is recognized as fresh/raw WCO which was collected from food restaurants and mostly disposed of without undergoing any proper treatment [21]. The collection of three types of WCO samples were denoted as WCO 1, WCO 2, and WCO 3. The three WCO types were represented as WCO 1 is four repeated time usage, followed by WCO 2 is three repeated time usage and WCO 3 is two repeated time usage. These WCO samples were differentiated based on the various frequent duration times WCO was used thereby exhibit different acid values as shown in Table 1. Based on the preliminary findings, the physical and rheological performance of modified binders with untreated WCO is affected by the different quality of acid value wherein the lowest acid value (WCO 3) achieved the most excellent performance, especially in regard to the binder rheological properties (G*/sin δ) in terms of rutting resistance. In contrast, the highest acid value, represented as WCO 1, has shown low binder performance. It can be summarized that the WCO possessed the lowest acid value exhibit good binder performance. Therefore, WCO 3, with the lowest acid value, was selected for further pre-treatment of WCO by conducting transesterification process in producing treated WCO to determine any performance improvement when the existing acid value was minimised through the chemical process.

Meanwhile, treated WCO is derived from the untreated WCO wherein this modifier underwent chemical treatment through the transesterification process. This chemical process is conducted when the untreated WCO is chemically reacted with methanol (alcohol) in the presence of sodium hydroxide (NaOH) as base catalysts to produce treated WCO. Prior to the process, a total of 1 mL NaOH and 600 mL of methanol were weighted and mixed together. Thereafter, this solution was added into 100 mL of untreated WCO in a beaker containing a magnetic stirring bar to ensure a homogeneous solution was obtained during the reaction. The 1:6 ratio (oil:methanol) was selected in the chemical process as the optimum ratio based on the source of the WCO which originated from the palm oil, the frequency times of the WCO used during the cooking process, and existing acid value quality. This factor influencing the selection of appropriate optimum ratio of oil:methanol. Besides, previous researcher proved that the usage of methanol is effective with ratio 6 to reduce acid value for untreated WCO. The minimization of acid value through the transesterification process is expected can enhance the physical and rheological performance of modified binder with treated WCO. The solution was heated on the hot plate until reached a temperature of 65 °C and the reaction was started for a duration time of 1 h. The reaction was completed when the separation of two major by-products was observed namely, treated WCO at the upper phase and glycerol in the lower phase.

Table 1 Acidity value content in WCO

Sample	Volume of KOH (ml)	Acid value (ml/g)	Conversion to FFA (based on oleic acid %)
WCO 1	31.7	3.55	1.78
WCO 2	25.3	2.83	1.42
WCO 3	14.8	1.65	0.83

Figure 1 showed the viscosity result at 135 °C on modified binder containing different WCO quality. The viscosity values decreased as WCO content increased. A similar trend was recorded for all the different WCO qualities and the viscosity decrement was sequentially observed from low quality (WCO 1) followed by WCO 2 and high quality of WCO (WCO 3). Modified binder incorporated with WCO is lower than control binder at 0.7 Pa.s due to the natural WCO characteristic which provided fluidity properties. Thus, induced the sliding effect of particles inside the modified binder. It can be seen that, WCO 1 sample displayed the highest viscosity result, which was 0.6 Pa.s for 3%, 0.5 Pa.s for 4% and 0.4 Pa.s for 5% of WCO and followed by WCO 2 sample which was 0.5 Pa.s (3%), 0.4 Pa.s (4%) and 0.3 Pa.s (5%), accordingly. The modified binder containing the 3%, 4% and 5% of WCO 3 sample recorded the lowest viscosity which was 0.3 Pa.s as compared to WCO 1 and WCO 2 samples.

It can be noticed that the highest different viscosity decrement was recorded by WCO 3, which indicated soft and less viscous characteristic in WCO 3 modified binder. Due to the softer binder, the lowest internal friction was produced, thereby decreased the flow resistance which affected to the lowest viscosity result. In economic aspect,

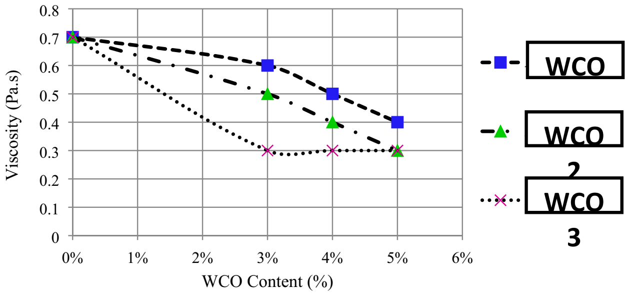


Fig. 1 Viscosity

low viscosity in binder is favourable due to low energy consumption with lower mixing, laying and compaction temperature thus save the construction cost (Sengoz & Isikyakar, 2008). The replacement of WCO in modified binder was beneficial for pavement construction by reducing the mixing and compaction temperature to minimise the operation cost.

The physiochemical properties of untreated and treated WCO are summarised in Table 2. Four main properties were examined, namely acid value, density, viscosity and water content. The transesterification process reduced the acid value from untreated WCO (1.65 ml/g) to treated WCO (0.54 ml/g). Meanwhile, treated WCO (0.81 kg/m^3) had a lower density as compared to the untreated WCO which was 0.89 kg/m^3. The density was predicted since the untreated WCO was thick relative to the treated WCO which was quite light in physical appearance. The viscosity result at temperature 135 °C for untreated WCO was significantly high (55.67 mpa.s) thus indicated the high internal friction. In contrast to treated WCO, which contained methyl ester, a lower viscosity was recorded as 1.15 mpa.s. Besides, the higher water content of treated WCO was observed as compared to untreated WCO. This is because the water was produced during the transesterification reaction. The noticeable difference between the two types of WCO was identified based on the color, in which untreated WCO was recognised as dark brown in colour while the treated WCO was light yellow.

Table 2 Physiochemical properties of untreated and treated WCO

Properties	Untreated WCO	Treated WCO
Acid value (ml/g)	1.65	0.54
Density (kg/m^3)	0.89	0.81
Dynamic viscosity (mpa.s)	55.67	1.15
Water content (ml)	0.085	6.46
Color	Dark brown	Light yellow

2.3 Hot Mix Asphalt (HMA) Incorporating with Untreated and Treated WCO in Modified Binders

Modified binders were prepared when the 5% of untreated WCO (at 5% optimum bitumen content) and treated WCO (at 4.9% optimum bitumen content) was added and mixed into the control binder (PEN 60/70). This percentage is selected based on the optimum value from physical test (penetration and softening point) and rheological test (Dynamic Shear Rheometer, DSR) among 0%, 5%, 10%, 15%, 20% of untreated and treated WCO, respectively as shown in Table 3. These materials were blended by using a high shear mixer at a constant speed of 1000 rpm for 1 h at 160 °C. Based on the physical result, the addition of higher percentage of untreated WCO content in binder increased the penetration value which indicates that the softer modified binders is produced thereby high tendency for rutting is expected. Meanwhile, the softening point is decreased when the untreated WCO is added which exhibit high-temperature susceptibility. The increasing trend of softening point was recorded for binder with treated WCO compared to untreated WCO contributed from similar polarity between binder and treated WCO attracted to one another forming a bonding connection which requires a higher temperature to break the carbon-hydrogen bond. Hence, explained the high softening point value for binder with treated WCO. The rheological findings show all the control and modified binder with untreated WCO sample achieved G*/sin δ value is less than 1 kPa which does not meet AASTHO T315 requirement (G*/sin δ should be ≥ 1 kPa). Basically, the value of G*/sin δ which is less than 1 kPa denoted that the modified binders can withstand for rutting tendency at maximum temperature which represented by failure temperature. The highest failure temperature achieved by control sample (PEN 60/70) compared to the modified binder containing untreated WCO indicates the improvement of rutting resistance thereby proved that untreated WCO modified binders

Table 3 Summary of physical and rheological test for control and modified binders

Designation	WCO content (%)	Penetration (dmm)	Softening point (°C)	G*/sin δ (kPa)	Failure temperature (°C)
Control (60/70)	*0%*	*68*	*49*	*0.78*	*70*
Untreated WCO	*5%*	*177*	*36*	*0.87*	*64*
	10%	236	29	0.66	58
	15%	245	20	0.77	46
	20%	228	15	0.76	46
Treated WCO	*5%*	*80*	*52*	*0.80*	*70*
	10%	82	51	0.74	70
	15%	84	51	0.79	70
	20%	101	50	0.55	70

prone to undergone deformation or rutting. This can be enhanced by using treated WCO in modified binder wherein the superior failure temperature is achieved comparable with control binder which is at 70 °C.

There were three different types of samples were tested for GC–MS in this research, wherein control binder, modified binders with 5% untreated WCO and 5% treated WCO. Thereafter, control binder and modified binders with 5% untreated WCO and 5% treated WCO were used for asphalt mixture production. There were three types of asphalt mixture were prepared for FESEM observation in which control mixture, 5% untreated WCO mixture, and 5% treated WCO mixture. For asphalt mixture preparation, control binder, modified binders containing 5% untreated WCO and 5% treated WCO together with the aggregates was heated at 130 °C and 110 °C. Then, binder-aggregates were mixed at 170 °C until the aggregate was coated well with the binder. After the mixing process, the bituminous mixture was compacted by using a Marshall compactor for 75 blow/face compaction standards for dense graded mixtures production. Based on the Marshall result, the highest Optimum Bitumen Content (OBC) value of 5.5% was achieved by control mixture, followed by the untreated WCO mixture with an OBC value of 5.0% and the lowest OBC value of 4.9% was recorded by treated WCO mixture. Once the OBC obtained, the actual asphalt mixture with the exact OBC percentages was prepared for further microstructure observation and mechanical testing for HMA containing untreated and treated WCO.

2.4 Experimental Methods

The experimental methods can be divided into three phases as presented in Fig. 2. In Phase 1, the polarity group classification is identified to investigate the compatibility of WCO in binder. The compatibility characteristic is measured by using GC–MS. Then, the adhesion between binder-aggregate is visualized by conducting FESEM in Phase 2. For Phase 3, the HMA containing untreated and treated WCO is evaluated for strength measurement by performing mechanical test (resilient modulus, dynamic creep and ITS) thus eventually strengthen the fundamental findings on how the compatibility of WCO in modified binders based on the polarity group identification affecting the adhesiveness properties between binder-aggregate in bituminous mixture.

2.5 Gas Chromatography–Mass Spectrometry (GC–MS) Test

The types of GC–MS used in this study is GC–MS (QP2010 Ultra Series) supplied from Shimadzu Malaysia Sdn. Bhd. GC–MS was performed to determine the quantitative analysis of chemical components in material for polarity group classification. This instrument comprises of gas chromatography (GC) coupled with mass spectrometry (MS) which enabling the separation, identification, and quantification of complex chemical compounds with low detection limit.

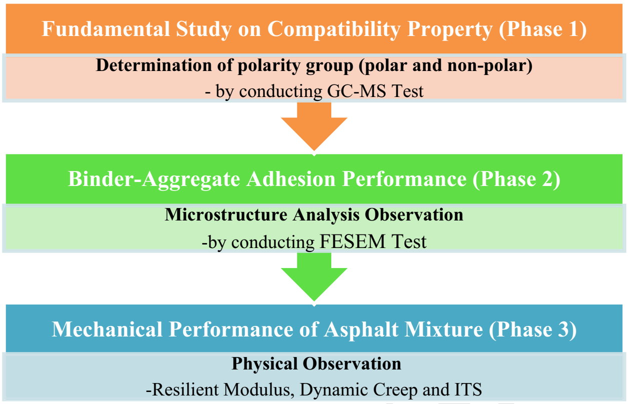


Fig. 2 Flowchart for Experimental Method (Phase 1, Phase 2, and Phase 3)

2.6 Field Emission Scanning Electron Microscope (FESEM) Test

The visualization of the surface morphology of the material was observed by using FESEM. The FESEM instrument used in this test is from the Hitachi SU8020 model. The test was performed in accordance with ASTM E 2090 [3] procedure. The material was sealed with tape on a metal stub during sample preparation. The prepared sample was coated with copper before putting into a gold coating machine. In obtaining a clear image, this material was vacuumed under the operation at 5.0 kV for 90 s. Then, the material was scanned up to 10,000× magnification and the visualization of morphological image structure was analyzed.

2.7 Resilient Modulus, Dynamic Creep, and ITS Test

In accordance with ASTM D7369-11, the elasticity behavior of the asphalt mixture after repetitive impact load was evaluated through the resilient modulus (M_R) test. This test provides an assessment of the resistance of the asphalt mixture to permanent deformation and its potential to return to its original condition after being subjected to 1000 kN loading. This test was carried out at 25 °C and 40 °C. The dynamic creep test was conducted by following the procedures outlined in ASTM D3497-2003. This test is recognized as the simplest method for assessing the permanent deformation resistance during service life. The sample mixture was tested for 3600 cycles at 40 °C and 60 °C for about 30 min. The highest creep stiffness of the mixture indicates a high resistance to rutting potential. The ITS test was performed in accordance with ASTM D6931-12. This test was conducted to assess the performance of the bituminous mixtures in terms of rutting and cracking potential. The ITS sample was conditioned by placing it in an air bath at 25 °C for a minimum of 4 h, prior to this test.

3 Results and Discussion

3.1 Determination of Polarity Group from GC–MS for Chemical Analysis

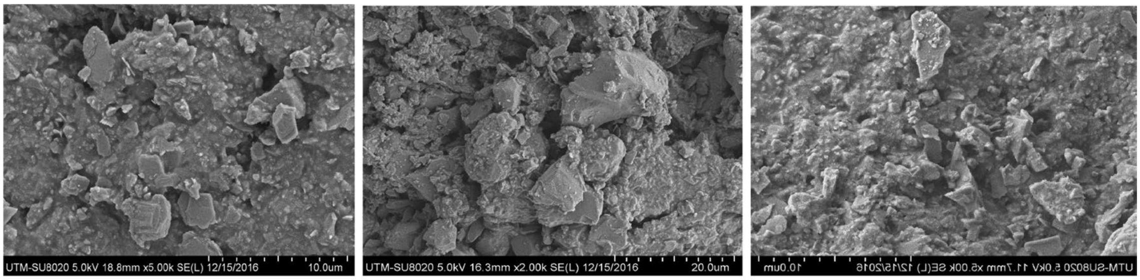
The molecule in the material can be classified into two different types of group namely, polar and non-polar. Uneven distribution of electrons which enable the electrostatic interaction to occur is identified as a polar group in which it consists of carboxyl, phosphate, amino, ketone, aldehyde, and hydroxyl. Meanwhile for the non-polar group, as recognized from the methyl group, the charges have cancelled out each other resulting no abundance of charges available at the opposite side thus recognized as symmetrical electron distribution. In principle, the combination of the similar group for instance polar-polar and non-polar-non-polar is allowable to make good chemical bonding. Nevertheless, the interaction between polar and non-polar group has no capability to chemically react with each other as the existence of distinct group interaction. Numerous components that existed in control binder are identified from carboxyl group which represented by 1,2,4-benzenetricarboxylic acid (-COOH-) as presented in Table 4. The presence of carboxylic acid observed from GC–MS indicates that the chemical composition was categorised as polar group. This is also supported by Robertson [28], which stated that the detection of carboxylic acid in binder constituent was categorized as a polar group and had high adhesiveness properties towards the dry aggregates. Meanwhile, the highest component presented in the modified binders containing untreated WCO were recorded by the components of Cyclotrisiloxane, hexamethyl ($C_6H_{18}O_3Si_3$) and Tetrasiloxane, decamethyl ($C_{10}H_{30}O_3Si_4$). The similarity presence of methyl (CH_3) between these two components was notable which indicates that the modified binders incorporating untreated WCO was categorised as a non-polar group. A noteworthy point that wants to be emphasized that the modification of binder with the addition of untreated WCO has given effect to the unstable and imbalance of chemical composition inside the material. This is due to the no attraction between the different polarity groups and refused to make chemical interaction. Thereby, it is proved that poor compatibility between these two materials as the non-equilibrium of chemical reaction existed between binder and untreated WCO due to the different polarity issue. The formation of ketone group (C = O) which represented as a polar group was mostly presented in modified binders containing treated WCO by the detection from 2,4,6-Cycloheptatrien-1-one, 3,5-bis-trimethylsilyl- ($C_{13}H_{22}OSi_2$) as similar with the chemical composition in the control binder. Overall, it can be summarized that modified binders with treated WCO was classified as a polar group. An equilibrium and stable chemical reaction was produced between control binder and treated WCO due to the similarity of polar group which induced an attraction between these materials. This indicated that the binder and treated WCO are compatible with each other, thereby improved the superior adhesiveness with the aggregate in asphalt mixtures.

3.2 Adhesion Between Binder-Aggregate for Structural Arrangement in Mixture from FESEM Microstructure Visualization

Figure 3 depicted the FESEM image for the control mixture, 5% untreated WCO mixture and 5% treated WCO mixture. Based on the microstructure image visualized by FESEM, the presence of more voids at certain points was observed for control mixture as compared to the treated WCO mixture. It can be noticed that the structure of control mixture less compacted in comparison with the treated WCO mixture due to the availability of voids in the bituminous mixture. This can be related with the natural property of the control binder which has high viscosity thus

Table 4 Chemical composition for control and modified binder with untreated and treated WCO

Types	Control binder (PEN 60/70)	Modified binders with 5% untreated WCO	Modified binders with 5% treated WCO
Molecule	1,2,4 benzenetricarboxylic acid	Cyclotrisiloxane, hexamethyl- Tetrasiloxane, decamethyl-	2,4,6-Cycloheptatrien-1-one, 3,5-bis trimethylsilyl-
Chemical Formula	-COOH-	CH_3	C = O
Area (%)	0.4805	0.4718 0.3737	0.5465
Polarity Group	Polar	Non-polar	Polar



Control Mixture 5% Untreated WCO Mixture 5% Treated WCO Mixture

Fig. 3 Microstructure observation visualized from FESEM image

affected to the low flow performance [19]. This is also supported by Hefer and Little [16], which stated that low flow performance affected the low coatability or wettability performance to coat the aggregates entirely thereby reduced the adhesion strength between binder-aggregate in the asphalt mixture. The incapability of control binder to coat or cover all areas in the bituminous mixture due to the low flow binder performance produced a non-uniform coating process. Therefore, it can be emphasized that the presence of voids in the control mixture was affected by the improper coating process of binder for the aggregates particles. The existence of voids caused the mixture to be un-compacted hence reduced the stability performance which affected the low mechanical strength relative to the treated WCO mixture. On the contrary, the high wettability potential of modified binders with treated WCO to coat the aggregates indicates the enhancement of flow performance due to the fluidity properties possessed by treated WCO.

For untreated WCO mixture, the existence of voids were very noticeable as compared to control and treated WCO mixtures. The increment of the gaps or voids existence in untreated WCO mixture was related to the reduction of the adhesion performance between the contacted materials due to the expectation of different polarity group interaction between modified binders with untreated WCO and aggregate surface. This was agreed by Xiao et al. [34] which stress out that the chemistry of the binder itself in terms of polarity and constitution influenced the interaction performance between binder-aggregate in the bituminous mixture. It can be proved that the structure arrangement of the mixture was affected by the polarity factor as the combination of polar and non-polar component has caused the disintegration of the particle in the mixture which leads to the de-bonding process between modified binders with untreated WCO and aggregate particles. Due to the incompatibility polarity group issue, it has effected the poor mechanical performance of untreated WCO mixture as well as compared to the other mixtures.

The surface microstructure for the treated WCO mixture illustrated in FESEM image indicates an improvement of the adhesion performance in the bituminous mixture whereby the modified binders with treated WCO exhibited better attraction to the polar surface aggregates. Another interpretation indicated that the similarity of polarity group contributes to the high affinity between polar modified binders containing treated WCO and polar aggregates. No existence of notable voids was observed in the bituminous mixture, and therefore it can be noticed that the treated WCO mixture was more compacted relative to the control and untreated WCO mixtures. The visualization of the compacted mixture from FESEM image proved that there was an improvement in the adhesion properties between the aggregates particles and modified binders with treated WCO.

3.3 Mechanism of Adhesion Between Bitumen-Aggregates Based on Microstructure Observation

The similar polarity groups induced the existence of a chemical interaction to occur wherein the polar reacted with other polar groups and vice versa. In contrast, the chemical reaction was not observed as no attraction existed between different polarity groups due to the internal molecule repulsion with each other to avoid chemical bonding interaction. The GC–MS result from previous analysis summarised that the control binder and treated WCO was categorised as polar group while on the contrary, non-polar group represented by untreated WCO as it exhibited hydrophobic behaviour [7]. This is also supported by Freemantle [14], which claimed that as the binder possess alcohol, amine, carboxyl, phenolic, and thiol, thereby it can be considered as a polar compound. According to Nurdin et al. [27], non-polar is recognised as hydrophobic (oil/fat loving) which is has a high solubility in fat source component only. In contrast, the polar group can be described as hydrophilic (water-loving) which can be dissolved in water. This theory is related to the common phenomena in which it can be observed that the oil (non-polar) based cannot be dissolved in water (polar) as the separation between oil at the upper layer and water at the lower layer is exhibited.

The modification of binder with untreated WCO had raised some polarity characteristic issues wherein the different polarity possessed by the control binder and untreated WCO caused the repulsion between the particles inside the material. It indicates that the refusal interaction occurs to form good bonding as the particle pushed between each other thereby caused the rupture, deterioration and weaken the chemical bond in modified binders thus lead to the decrement of cohesive strength in the materials. It has to be emphasized that the compatibility properties between binder and untreated WCO were reduced due to the interaction of different polarity group which resulted in adverse rheological performance as evidenced by the poor rutting resistance with lowest failure temperature [9]. Testing for universal sorption device (USD) conducted by Guarin et al. [15] discovered that the stone surface was categorised as polar which had a high affinity towards polar liquid. This is supported by Volpe and Siboni [32] and Bhasin and Little [11] which confirmed that the aggregates surface derived from polar group naturally. An attraction between molecules in the modified binders containing treated WCO and the polar surface of aggregates was existed due to the similarity of polar groups thereby increased the adhesion performance of the binder-aggregates in the bituminous mixture [14]. However, the opposite polarity group possessed by the modified binders with untreated WCO, being a non-polar group, reduced adhesion to the polar surface of aggregates because no attraction bonds existed owing to the different polarity groups thus led to debonding. It can be summarized that the polar attraction between molecules in the asphalt binder and polar surface of the aggregates influenced an improvement of superior adhesion performance between binder-aggregates interactions. In contrast, a notable different polarity group has worsened the adhesion binding performance of modified binders with untreated WCO for coating the aggregates.

3.4 Mechanical Performance Evaluation Through Resilient Modulus, Dynamic Creep and ITS for HMA

The summarised results for the resilient modulus of control, 5% untreated WCO and 5% treated WCO mixtures which were tested at 25 °C and 40 °C is illustrated in Fig. 4. Based on the result, an increment of M_R was achieved from 2681 MPa for untreated WCO mixture to 5977 MPa for treated WCO mixture in which it indicated that the chemical modification enhanced the resilient modulus performance. Surprisingly, the obtained results showed that the mixes containing treated WCO exhibited superior results to the control mix sample by exceeding the resilient modulus for the control mixture at 5006 MPa. Besides, the resilient modulus was reduced at 40 °C temperature as compared to 25 °C, which was recorded as 601 MPa for untreated WCO mixture, 915 MPa for control mixture and 1214 MPa for treated WCO mixture. This indicated, as expected, that the treated WCO mixture achieved the highest resilient modulus when compared to the other mixtures. According to this trend, it shows that treated WCO mixture exhibited the highest achievement of resilient modulus, while the lowest resilient modulus was recorded by untreated WCO mixture at both temperatures.

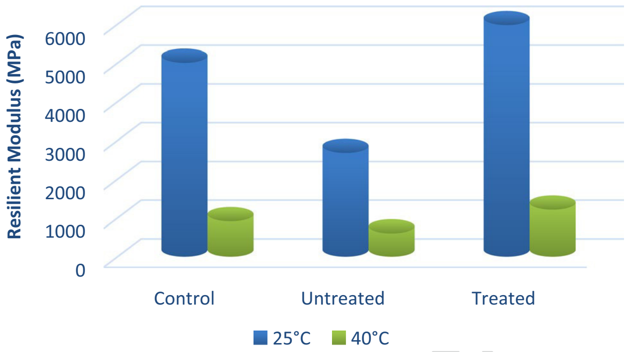


Fig. 4 Resilient modulus (M_R) for control and modified mixture containing untreated and treated WCO

Table 5 The independent samples t-test for resilient modulus

Independent samples test		Resilient modulus	
		Equal variances assumed	Equal variances not assumed
Levene's test for equality of variances	*F*	23.386	
	Sig	0.000	
t-test for equality of means	*t*	7.333	7.333
	df	16	8.523
	Sig. (2-tailed)	0.000	0.000
	Mean difference	3644.333	3644.333
	Std. error difference	496.947	496.947
	95% confidence interval of the difference		
	Lower	2590.853	2510.506
	Upper	4697.814	4778.160

An independent *t*-test analysis was performed to compare the resilient modulus performance between control, untreated WCO and treated WCO mixtures at two different temperatures of 25 °C and 40 °C, respectively as shown in Table 5. The Levene's test for equality of variances showed that the population variance was equal based on the Sig. value of 0.000. Besides, the t-test for equality of means recorded the 2-tailed value for 0.000, which is less than 0.05. Since $p < 0.05$, therefore the null hypothesis was rejected. Another interpretation indicated that a difference of resilient modulus results between control, untreated WCO, and treated WCO, at both temperatures, was statistically significant.

Figure 5 presents dynamic creep stiffness results which conducted at both temperature of 40 °C and 60 °C. The increment of creep stiffness at 40 °C was recorded from untreated WCO mixture (196.15 MPa), control mixture (264.29 MPa) and treated WCO mixture (330.40 MPa). This implied that the treated WCO mixture exhibited the highest achievement of creep stiffness as compared to the control and untreated WCO mixtures. In addition, it proved that the rutting resistance was improved in treated WCO mixture as evidenced by the increased of creep stiffness strength. The improvement of creep stiffness in treated WCO mixture indicated a high rutting resistance, thereby reduced the tendency of permanent deformation to occur. Besides, the decrement of creep stiffness was noticed at 60 °C temperature as compared to 40 °C. However, the result reported a conflicting finding with temperature 40 °C, in which the control mixture achieved the highest creep stiffness for 85.96 MPa at 60 °C. In contrast, the creep stiffness result was recorded slightly lower for treated WCO (16.04 MPa) and untreated WCO mixtures (11.33 MPa) in comparison with the control mixture.

The data was further extensively analysed by an independent t-test analysis to compare the creep stiffness performance for control, untreated WCO and treated WCO mixture samples for different test temperatures at 40 °C and 60 °C, correspondingly as presented in Table 6. The null hypothesis stated that the mean creep stiffness for three different types of mixture at low temperature (40 °C) and high temperature (60 °C) was equal (Ho: $\mu_{40\,°C} = \mu_{60\,°C}$). The 2-tailed value was recorded as 0.000 which is less than 0.05, hence the null hypothesis was rejected. This implied that the mean difference of creep stiffness for control, untreated WCO and treated WCO mixtures at both temperatures of 40 °C and 60 °C was statistically significant.

Table 6 The independent samples *t*-test for creep stiffness

Independent samples test		Creep stiffness	
		Equal variances assumed	Equal variances not assumed
Levene's test for equality of variances	*F*	1.188	
	Sig	0.292	
t-test for equality of means	*t*	9.894	9.894
	df	16	13.392
	Sig. (2-tailed)	0.000	0.000
	Mean difference	225.84889	225.84889
	Std. error difference	22.82732	22.82732
	95% confidence interval of the difference		
	Lower	177.45712	176.67988
	Upper	274.24066	275.01790

The ITS which tested at 25 °C is demonstrated in Fig. 6. ITS result shows that untreated WCO mixture was represented as 678 kPa, which was recorded lower as compared to the control mixture (1211 kPa) and treated WCO mixture (1349 kPa). This implied that the treated WCO mixture exhibited the highest tensile strength while the lowest tensile strength was recorded by untreated WCO mixture. This attraction increased the adhesion of the modified binder with treated WCO to the aggregates and led to the good bonding between the materials. In the bituminous mixture, the contact point between the aggregate particles was observed when the bitumen held the aggregate skeleton in position. This result implied that the presence of the binder produced an efficient aggregate binding that reduced the tendency of flow movement of the bituminous composition in the mixture, thereby increasing the strength performance of the

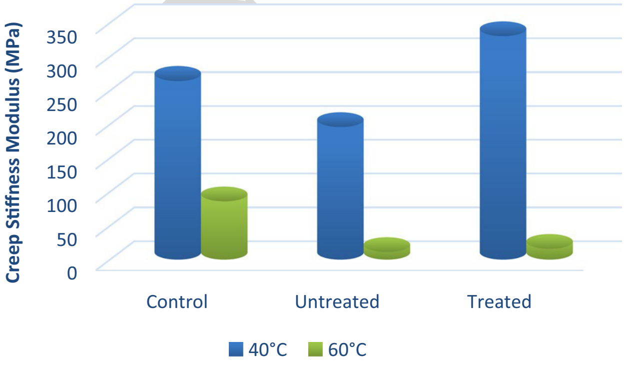


Fig. 5 Dynamic creep stiffness for control and modified mixture containing untreated and treated WCO

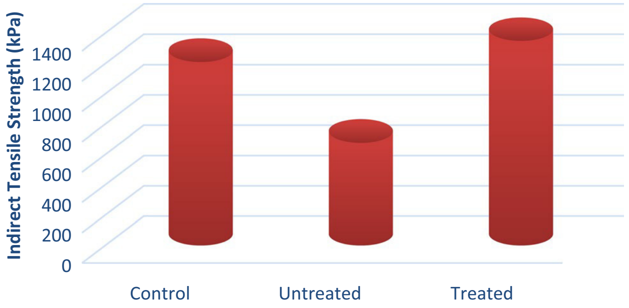


Fig. 6 ITS result for control and modified mixture containing untreated and treated WCO

Table 7 One way ANOVA for ITS

Source	Sum of squares	*df*	Mean square	*F*	*p*
Between groups	753,374.000	2	376,687.000	1855.601	0.000
Within groups	1218.000	6	203.000		
Total	754,592.000	8			

treated WCO mixture. In summary, the better performance of tensile strength was recorded by treated WCO mixture as compared to the control and untreated WCO mixtures, which directly proved that the chemical treatment had enhanced the treated WCO performance in asphalt mixture.

A statistical analysis by using SPSS software was conducted for control and modified mixtures incorporating untreated and treated WCO as shown in Table 7. The data were analysed based on the 95% confident interval ($\alpha = 0.05$). The one-way independent analysis of variance (ANOVA) was performed to evaluate the significance of different asphalt mixture samples, namely control, untreated WCO and treated WCO mixtures on the indirect tensile strength (ITS) performance. The null hypothesis for analysis was that the mean of different mixture samples for ITS was equal (Ho: $\mu_{\text{control mixture}} = \mu_{\text{untreated wco mixture}} = \mu_{\text{treated wco mixture}}$). The ANOVA result displayed implied that there was a statistically significant difference in indirect tensile strength exhibited by the different asphalt mixture which consisted of control, untreated WCO and treated WCO mixtures as evidenced by the *p* value as 0.000. Hence, the null hypothesis was rejected since the p-value was less than 0.05 and indicated that the ITS performance was influenced by the different types of mixes namely control, untreated and treated asphalt mixture.

4 Conclusion

The GC–MS result discovered the identification of polar compounds in control binder and treated WCO while untreated WCO was recognised as a non-polar compound according to the chemical composition analysis. Based on the determination of polarity group, an incompatibility issue was identified and raised between binder and untreated WCO thereby justified how this polarity group contribute to the low adhesion bonding performance between modified binders with untreated WCO and aggregate. The decrement of adhesion properties was affected by the different polarity group between aggregate and modified binders with untreated WCO thus lead to the adverse mechanical performance in the untreated WCO mixture. Meanwhile, the FESEM image illustrated that non-existence of voids is observed for treated WCO mixture thereby exhibiting more compacted arrangement as compared to the control and untreated WCO mixtures. It can be noticed that, an improvement of the adhesion performance between the modified binders containing treated WCO and aggregate is attained as evidenced by the compact structure arrangement in bituminous mixture. Meanwhile, the presence of voids were noticeable in untreated WCO mixture which attributed to the interaction of different polarity group between untreated WCO (non-polar) and polar surface aggregate. The reduction of adhesion bonding performance between the contacted materials was influenced by the interaction of opposite polarity group thus produced the notable gap/voids in the untreated WCO mixture. The relationship between fundamental theory on compatibility property based on the polarity group and adhesion of binder-aggregate is proved from mechanical test in which superior performance was recorded by treated WCO mixture compared to control mixture and untreated WCO mixture based on the highest strength obtained for resilient modulus, creep stiffness and ITS.

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