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EVALUATION OF POLYMER AND NANOMATERIALS MODIFIED ASPHALT BINDERS AND MIXTURES: A COMPARISON APPROACH

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Supervisor

ASSOC. PROF. DR. SHABAN ISMAEL ALBRKA

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APPROVAL

We certify that we have read the thesis submitted by Emmanuel Acquah titled “EVALUATION OF POLYMER AND NANOMATERIALS MODIFIED ASPHALT BINDERS AND MIXTURES: A COMPARISON APPROACH” and that in our combined opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Applied Sciences.

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DECLARATION

I hereby declare that all information, documents, analysis and results in this thesis have been collected and presented according to the academic rules and ethical guidelines of Institute of Graduate Studies, Near East University. I also declare that as required by these rules and conduct, I have fully cited and referenced information and data that are not original to this study.

Emmanuel Acquah

10/01/2022.

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Emmanuel Acquah

ABSTRACT

Evaluation of polymer and nanomaterial modified asphalt binders and mixtures: A comparison approach

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This comparative study was to assess the influence of polymers and nanoparticles on the physical and rheological properties of asphalt cement. Four different modifiers, namely; Epoxidized Natural Rubber (ENR), Acrylate Styrene Acrylonitrile (ASA), Nano-Alumina (Al_2O_3) and Calcium Carbonate ($CaCO_3$), were added to unmodified asphalt cement at 5% of the weight of the asphalt. The similarities and differences that occurred from the storage stability test, viscosity test, and frequency sweep were thoroughly examined. There was improvement in the rheological properties of the asphalt cement at intermediate and high temperatures. There were no storage stability problems at high temperatures when the modifiers were introduced, indicating that all the binders exhibited good compatibility and good workability properties. The asphalt cement containing 5% ASA recorded the highest penetration resistance. The modified binders had relatively higher softening points compared to the unmodified binder, with 5% ASA recording the highest softening point temperature of 56°C. It was observed that at a predetermined temperature on the viscosity/temperature scale, the viscosity of the modified binders was higher, which means there was better rutting resistance at high temperatures. 5% ENR had the highest complex modulus (G*) values, which illustrates that the binder had the greatest tendency to resist any applied stress. 5% Al_2O_3 had the greatest toughness among the modifiers. The modified asphalt had higher failure temperatures when compared to the unmodified asphalt cement. It is therefore imperative to acknowledge that these asphalt modifiers significantly alter the overall performance and functioning of any asphalt pavement.

Keywords; Asphalt binder, Nanoparticles, Polymer, Rheology, Rutting

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LIST OF ABBREVIATIONS

Al_2O_3	Nano-Alumina
ANN	Artificial Neural Network
ANFIS	Adaptive Neuro - Fuzzy Inference System
ASA	Acrylate Styrene Acrylonitrile
$CaCO_3$	Calcium Carbonate
ENR	Epoxidized Natural Rubber
GPR	Gaussian Process Regression
HMA	Hot Mix Asphalt
MAE	Mean Absolute Error
PG	Performance Grade
PV	Pressure Vessel
RMSE	Root Mean Square Error

CHAPTER I

Introduction

Bitumen is an old engineering material that has been in existence for decades (Cong, 2020; Yao et al., 2012). It has a varied application ranging from acting as a water repellent to insulating and sealing purposes in a variety of housing materials, such as paints and joint sealants, among others. Notable among its uses is its application in the paving industry (Yildirm, 2007). It has been used as a binder in combination with mineral aggregates to produce asphalt concrete, which has become the preferred choice nowadays for road paving purposes such as runways, highways, and parking lots, just to mention a few (Alhamali et al., 2015; Chen et al., 2002; Madhi et al., 2013).

Although in the production of asphalt concrete a limited quantity is used, bitumen plays a significant role in the overall property and performance of the produced asphalt mixture. Depending on the prevailing temperature, bitumen can be described as a viscoelastic liquid at elevated temperatures or a viscoelastic solid at low temperatures, which tends to be brittle and crack up with the application of external stresses (Madhi et al., 2013, Mubaraki et al., 2016, Yao et al., 2012). That being said, it is worth noting that the resulting properties of the asphalt are highly dependent in part on the chemical properties of the base bitumen and also on the type of modifier used in the modification process. Undoubtedly, the use of bitumen for road construction has skyrocketed over the years because of these desirable qualities that will be enumerated (Cong et al., 2020; Mubaraki et al., 2016; Steyn, 2011; You, 2011). Firstly, rapid construction is achieved when asphalt paving is considered, as it eliminates the time of curing experienced in concrete paving. This has the added advantage of being opened to traffic a few hours after construction, since there is no waiting time for strength development, and therefore there are fewer blockages on the roads to inconvenience motorists (Yildirm, 2007). Secondly, a safer driving surface is achieved. When good construction practices are followed, roads paved with asphalt produce smooth surfaces, which allow for a safer and more comfortable experience when driven upon. This smooth sensation and experience has the added advantage of decreasing the rate of wear and tear of the vehicle tires, making it cost effective as far as road pavement is considered (Yang 2013). Thirdly, it leads to energy efficiency because the smooth surface of the pavement leads to less rolling resistance between the tire and the pavement surface. As a result, fuel economy improves and emissions and pollution are reduced (Xiao, 2014). Lastly, low maintenance is required when asphalt is correctly laid because there are practically no joints in its construction, minimizing the likelihood of defects occurring from faulty joints (Yildirm, 2007).

While all the above benefits have been highlighted, the use of asphalt in paving is not without some drawbacks. Most of the distress experienced on asphalt pavements can be attributed to repeated application of traffic load, extreme weather conditions, especially precipitation and temperature, poor quality materials used in the construction, improper construction practices adopted and inadequate maintenance (Ali, et al., 2016). Defects such as rutting, thermal cracking, fatigue cracking, bleeding, slippage cracks, etc. are common failures experienced in asphalt pavements that make them less durable (Cong, et al., 2020; Kumar & Veeraragavan, 2011; Slowik, 2017). Rutting is the permanent, distinct and noticeable surface depressions or grooves in the wheel path of vehicles resulting from repeated loads during elevated service temperatures. This usually occurs in the hot season when high temperatures are recorded because there is a reduction in the binder viscosity (Al-Mansob, et al., 2017; Nejad, et al., 2016). Thermal cracking is an asphalt defect that can be linked to the low temperature of the environment common in cold regions. This defect is characterized by the formation of almost equally shaped cracks oriented in an orthogonal direction to the pavement's centerline (Al-Mansob, et al., 2017; Asmael & Waheed, 2018). Fatigue cracking is generally load-related and arises when the pavement experiences failure in the form of small interconnected cracks as a result of repeated vehicular stresses. This defect is accelerated by factors such as aging and inadequate drainage (Jahromi & Khodaii, 2009).

Road construction is a massive investment that requires massive capital to ensure its successful completion, so they should be able to last as long as possible with as little maintenance as possible. Numerous studies have been carried out to seek better ways to enhance their desired qualities or properties (Cong, et al., 2020; Kumar & Veeraragavan; Slowik, 2017). In the process of ameliorating and enhancing these desirable qualities, modifiers have been introduced into asphalt mixtures because they have been documented to help mitigate some of the distress in asphalt pavements. These modifiers are great at tackling the permanent deformation from extremely higher temperatures like rutting and lower temperature defects like thermal cracking and fatigue cracking from repeated vehicular loads or stresses (Becker & Rodriguez, 2001; Huang, 2010; Jahromi & Khodaii, 2009). Since it is evident that when an ideal modifier is selected, it positively changes the failure properties of the binder such that it is able to yield better to applied stresses before it fails, it is important that selecting a suitable modifier in asphalt modification is very crucial considering the engineering and economic perspective (Yildirm, 2007).

Problem statement

The stresses as a result of traffic and loading, climatic conditions, and material characterization have led to defects such as rutting, cracking, stripping, shoving, etc., making the asphalt pavements deteriorate faster than expected. In this comprehensive study, a critical assessment will be undertaken to access the similarities and differences occurring in the use of polymers and nanoparticles as modifiers in asphalt binders since they significantly improve the physical and rheological properties of the binder, such as greater ductility, greater resistance to rutting and cracking, etc., thereby helping to eliminate the aforementioned defects.

Aim of the study

Although numerous research and studies have been carried out on the characteristics of polymers regarding their performance in asphalt binders and mixes, little focus has been placed on correlating and comparing these modifiers. This comparative study aims to compare the influences of polymers and nanoparticles on the physical and rheological properties of bitumen binder.

Significance of study

This study seeks to provide a comprehensive assessment of four (4) different modifiers in asphalt binders and mixtures by comparing the similarities and differences occurring in the physical and rheological properties as well as the engineering properties of these modifiers. The results provided in this study will provide in-depth information to the industrial sector regarding the use of these modifiers

Limitation of the study

There was difficulty getting relevant information on other commonly used polymers and nanoparticles, which could have helped generated a more holistic conclusion.

CHAPTER II

Literature review

Both online and manual searches were employed in order to find suitably related literature for this study. Although there seems to be sizable information relating to some polymers or other modifiers, there seems to be limited research work involving the comprehensive evaluation of two (2) or more of these modifiers. Again, since the use of nanomaterials is a fairly new technology in the road pavement sector, little research and information was readily available. This research, reviews, and experiments provided the needed and crucial information upon which this present study was successfully achieved.

Asphalt concrete background

Asphalt concrete is a composite material that is extensively used in the pavement industry for the construction of numerous projects such as runways, parking lots, interstate highways, etc. This composite material is basically made of two primary constituents, namely aggregates and bitumen binder. Aggregates used in the manufacture of asphalt concrete could be fine, coarse, natural, manufactured or a combination of these, and they account for about 90–95% of the total weight of the asphalt concrete (Galooyak, et al., 2010; Ghile, 2006; Habbouche, et al. 2018; Kumar, et al., 2011). Based on the asphalt mixes, asphalt concrete could be described as dense graded, open graded, or gap graded. Dense graded asphalt mixes are manufactured from well graded aggregate gradation and mostly adopted for general use. Because it has the optimum quantity and gradation of both fine and coarse aggregates, dense graded asphalt is highly impermeable. Depending on the volume or quantity of the different types of aggregates present in the mixture, dense graded could be further classified as either fine-graded or coarse-graded mix. Open graded asphalt mix, on the other hand, is achieved by adopting a relatively uniform aggregate particle size and distribution in the manufacture of the asphalt concrete. Because of the absence of smaller aggregates to fill the voids between bigger particles, this type of mix is relatively permeable, so its use is mostly specialized and used in areas where rapid drainage from the pavement surface is required. Special care is needed when adopting pavement construction to prevent rainwater and other forms of precipitation from seeping into the underlying layers. The gap graded mix is achieved in a similar way as the dense graded mix, but with this type, there is a minimal amount or absence of intermediate aggregates. This aggregate size selection type makes the gap graded mix more permeable than the dense graded (Yuan, et al., 2021).

Asphalt concrete could further be classified as hot mix asphalt (HMA), cold mix asphalt, warm mix asphalt mix, and "cut-back" asphalt, depending on how the mixture is prepared and laid on site. HMA is manufactured by heating the bitumen binder to temperatures of about 150 °C and then thoroughly mixing it with the aggregates (fine and coarse), which is then placed and compacted in place while still in its hot state. This asphalt concrete is recommended for use on pavements that are subject to high stresses and loading as a result of vehicular traffic, such as highways, intersections, and so on. Cold mix asphalt mixes are usually produced by thoroughly mixing emulsified bitumen with aggregates, which is then placed and compacted at an ambient temperature. A bitumen emulsion is a liquefied suspension product in which bitumen is suspended in a finely divided condition in an aqueous medium and stabilized by an emulsifying agent. The bitumen content in the emulsion is around 60% and the remaining 40% is water (Roberts, et al. 1996; Transport Research Board 2000). Unlike HMA, cold mix asphalt is used in areas where the stresses imposed on the pavements are minimal with low volume traffic, as they are not resilient enough to take heavy loads. They are therefore suitable for the construction of rural roads, remedial works like patching on roads, etc. Warm mix asphalt has properties and characteristics similar to HMA, but with this asphalt mix, the heating temperature is lower. The mixture, comprising of the bitumen binder and the aggregates, is adequately mixed, placed and compacted while still warm, which is usually above the surrounding temperature. Its use is recommended in areas where traffic is not very high. It is also good for use in pavement repair work. Asphalt cutback may be classified as slow-curing, medium-curing, or rapid-curing, depending on the solvent used in the production of the asphalt. This asphalt type is used mostly as a surface treatment and in cold-laid plant mixes. Slow-curing asphalt can be obtained directly through the distillation process of crude oil or by "cutting back" asphalt cement with a heavy distillate, such as diesel oil. They have lower viscosities and harden slowly as the petroleum solvent gradually evaporates. Medium-curing asphalts are obtained by fluxing the residual asphalt with a light fraction of petroleum solvent such as kerosene. Unlike the slow-curing type, medium-curing cutback asphalts harden faster and have higher viscosity, although the consistencies of the different grades are similar to those of the slow-curing asphalts. Rapid-curing cutback asphalts are produced by thoroughly mixing asphalt cement with a lighter petroleum distillate that evaporates easily, thereby facilitating quick curing and placing. Petroleum solvents such as gasoline are generally used in this type of cut-back. This type of asphalt can be used for pavement remedial works, on-site highway pavement surfaces, and is relatively more durable compared to the other "cut-backs". (Paige-Green, et al., 2005; Roberts, et al., 1996; Transport Research Board 2000)

Polymers as modifiers

The most common asphalt modification over the years has been the use of polymers. Polymers are large molecules formed by the chemical bonding of long repeating chains of smaller units called monomers. These monomers may just be an atom or two or a complicated, complex-shaped structure containing a dozen or more atoms. Generally, polymers come in many forms, but the most common and distinct forms include the straight chain and the complex variations of linked and cross-linked blocks. Polymers may exist naturally or artificially synthesized and are made of thousands of atoms, which have been observed to directly affect their melting and boiling points. The longer and heavier the polymer, the higher its viscosity, boiling point, and melting point will be. Polymers have greater surface areas, which enables them to easily bond with other molecules, enabling them to form giant complex structures. Although some polymers may have similar building units or monomers, their overall properties will be different from one another because the monomers may be linked differently together (Behnood, et al. 2018; Kumar, et al. 2011). Polymers may be classified as elastomers, plastomers, crumb rubber or reactive polymers. Elastomers are a group of polymers that behave like rubber, meaning they are very elastic and are usually lightly cross-linked (Xiao, et al. 2014). Common examples of this group include Styrene–butadiene elastomers (linear or radial) SBS, Styrene–butadiene rubber (SBR), Styrene–isoprene–styrene elastomers (SIS), Styrene–ethylene–butadiene–styrene elastomers (SEBS), and Styrene–butadiene elastomers (SBE). The second group, called the plastomers, has both plastic and elastic properties, with examples being ethylene–vinyl acetate (EVA), ethylene–methyl acrylate (EMA), Ethylene–butyl acrylate (EBA), atactic polypropylene (APP), polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC). Crumb rubber is very elastic and is mostly acquired from ground car tires. Reactive polymers used in bitumen modification are those polymer modifiers which are believed to chemically react (rather than physically mix or interact) with some components of bitumen, e.g., reactive ethylene polymers and isocyanate-based polymers. Rubber is a naturally occurring fluid obtained from the sap of the rubber plant. In this state, it is processed in the rubber industry and used in the manufacture of items such as tires, rubber shoes, adhesives, gloves, etc. Although it has numerous uses when processed, its usage is still limited because of its low temperature susceptibility, rapid degradation by oxidation, and high solubility in hydrocarbons, organic solvents, and oils. To limit its drawbacks and increase its usage, natural rubber is usually epoxidized by chemical modification to produce epoxidized natural rubber (Ismail, et al.2010; Sid, 2017).

Styrene Butadiene Styrene (SBS) Polymer

This is among the most commonly used modifiers in asphalt modification and is classified under the group of elastomers. Since its introduction in the pavement industry, numerous advantages have been recorded when incorporated into asphalt binders as modifiers, although some drawbacks have also been encountered. SBS may be radial, linear, or branched copolymer depending on how the other molecules get bonded to the styrene "backbone" (Behnood, et al. 2018, Chen, et al. 2007). This bonding to the "backbone" structure slightly differentiates how these copolymers behave. The major drawback to its usage is that there have been known stability problems when stored at high temperatures over a given period of time. This has therefore created the need to introduce other stabilizing agents such as sulphur to help mitigate the aforementioned drawback associated with its use. The stabilizer works by chemically creating a crosslink to stabilize the reactive moieties found in the SBS copolymer (Chen, et al. 2007; Inigo, et al. 2014). Although the drawback of using SBS copolymer cannot be completely ignored, it is still among the preferred modifiers due to its ability to alter the bitumen to resist rutting at high service temperatures, improve the temperature susceptibility of asphalt and increase flexibility at low temperatures (Slowik, 2017; Sun, et al. 2007).

Styrene Butadiene Rubber (SBR) Polymer

This is another relatively cheaper elastomer that is widely used in pavement construction. It is a copolymer where styrene and butadiene molecules combine chemically to form giant molecules with multiple or complex units. They may be classified as either emulsion SBR or solution SBR with other molecules such as free radicals and stabilizers found in them (Britannica 2018; Speight, 2020). Elastomers have the unique ability to maintain their initial shapes after being subjected to loading. Aside from the high elasticity exhibited by SBR, it has other unique attributes such as increased resistance to high temperature rutting and shoving, increased heat-aging resistance, and better abrasion resistance. The major drawback with the use of this polymer is that because of the double bonds found in its "skeleton", they are easily prone to degradation by oxidation, which makes them more brittle and have poor solvent resistance (Polymer handbook vol.8). Despite this, it is widely used because it has other useful properties that natural rubber does not. They have high tensile strength, but their final properties are greatly influenced by the ratio of the styrene and the butadiene present in the mixture (Becker, 2001; Saboo, & Kumar, 2016).

Natural Rubber (NR)

This is a biodegradable, non-synthetic elastomer used in pavement construction. It is predominantly obtained from the tropical rubber plant, Hevea Brasiliensis, which is milky white when freshly harvested. The forming blocks are the isoprene monomers. Natural rubber is relatively cheaper and easier to access compared to other polymers. To enhance its use and limit the drawbacks associated with its use, NR is normally vulcanized, which has been documented in previous studies to produce some desirable effects on the overall performance of the rubber (Puskas, et al. 2014; Rubber polymers, 2020). It has good fatigue resistance at low and ambient temperatures. When used in a temperature range of 50 °C to 100 °C, they have good resistance to abrasion, good ductility, and good tensile strength. NR is entirely made of cis–1,4 repeating polymer and its properties change when the proportions of cis–1,4 are varied. There is increased mechanical strength, a decrease in glass transition temperature, and increased crystallinity when the proportions of cis 1,4 are increased. The major uniqueness of this polymer is its ability to return to its initial form when the loading acting on it is removed, making it highly extensible (Britannica 2018). They are easily degradable when they come into contact with hydrocarbon-based solvents, fuels, oils, and other non-polar solvents. Its use is limited because of drawbacks such as poor heat resistance and being easily degradable by oxidation associated with its use (Polymer handbook vol.8; Rubber Polymers, 2020).

Ethylene Vinyl Acetate (EVA) Polymer

It is a synthetic semi-crystalline plastomer which is made up of a copolymer of ethylene and vinyl acetate molecules. The property exhibited by the plastomer is directly linked to the proportion of ethylene and vinyl acetate molecules present (Airey, 2002; Saboo, & Kumar, 2016). Desirable attributes of EVA plastomers include increased stiffness and improved elasticity at high temperatures. Unlike elastomers that have a flexible "backbone" structure and basically resist deformation by stretching and returning to their previous state when the loading is removed, plastomers are characterized by the rigidity of their backbone, enabling them to resist deformation when loaded. They have the added advantage of improving the workability of the mix when used as a modifier (Airey, 2002), by increasing the softening point, stiffness, and viscosity of the asphalt mix. They are crystalline at ambient temperatures. Previous studies have shown that using EVA plastomer at an optimum amount can significantly improve the mechanical and rheological properties of the asphalt mix (Janmohammadi, et al. 2020).

Nanoparticles as modifiers

A nanomaterial may simply be defined as a material with a dimension falling between 1 and 100 nm. Its form may vary from particles, tubes, rods, or fibers. Due to their extremely small size and greater surface area, their behavior as a bulk unit is quite different from that exhibited by normal-sized materials (Krshnamort, et al., 2007; Ramadhansyah, et al. 2020; Steyn, 2011; Yang, et al.2013; Zangena, 2019). Their small particle sizes and having a high surface area to volume ratio give rise to high reactivity in chemical reactions. Examples of commonly used nanoparticles in asphalt modification include nano-silica, nano-clay, carbon nanotubes, nano-titanium, nano-alumina, etc. With the addition of nanoparticles to the neat binder, the overall mechanical and physical properties are altered to better perform under traffic loading or when subjected to extreme weather conditions. The qualities when nanoparticles are introduced in asphalt modification include increased resistance to deformation both at high and low temperatures, better resistance to moisture penetration, enhanced elasticity, better aggregate retention, and high durability (Ramadhansyah, et al. 2020; Yao, et al. 2012).

Nanoclay

Nanoclay is a type of nanoparticle consisting of mineral silicates in a layered structure. Nanoclay can be classified under many groups depending on its morphology and chemical composition. These groups include bentonite clay, kaolinite clay, montmorillonite, hectonite, vermiculate, and halloysite (Jahromi, & Khodaii, 2009; Partl, et al. 2004; Ren, et al. 2020). The commonly used type of nanoclay is the montmorillonite nanoclay, which is plate-like and consists of aluminium silicate layers. When montmorillonite is dispersed in a polymer matrix, its surface modification allows it to form nanocomposite. Halloysites are two-layered matrices that are hollow tube-shaped and are also used in modifying asphalt rheology. The use of nanoclay has gained increased research over the last decade owing to its effect on the asphalt mix when added to other compounds, either as a catalyst or a modifier. The use of nanoclay in the construction industry has shown to significantly improve the physical and rheological properties of asphalt (Ghile, 2006; You, et al., 2011).

Nanoalumina particle

This may be spherical or nearly spherical with branched fibers. The general property of this modifier is largely dependent on the proportion of the aluminium and oxygen compositions. They have good thermal and mechanical properties, and improved strength and toughness (Yang & Tighe, 2013). In recent years, there has been an increase in research to better understand the properties exhibited by these nanoparticles and how to effectively utilize them. The properties of the bulk alumina are entirely and uniquely different when compared at the nano level and have a high surface area to volume ratio (Ismael, et al.2016; Zangena, 2019). Previous studies in this field suggest that when incorporated into the asphalt mix as a modifier, there is increased stiffness in the binder, improved temperature susceptibility, improved elastic properties, increased resistance to thermal rutting at high temperatures, and fatigue resistance at intermediate temperatures. The physical and rheological properties of the asphalt mix are greatly enhanced when nanoalumina is added (Calandra, et al., 2020; Galooyak, et al., 2010). With all these successes recorded above, nanoalumina has its fair share of drawbacks. There is agglomeration between the nanoalumina particles and the bitumen, which results in part from the high surface energy of its particles (Bhat & Mir 2021).

Nanosilica particle

This is among the cheapest nanomaterials to be used as a modifier in asphalt, which makes its usage affordable. Like other nanoparticles, nanosilica is also characterized by having a high surface area to volume ratio. Several advantages of using nanosilica have been documented, including increased rutting resistance at high service temperatures, resistance to fatigue cracking, easy dispersion in asphalt to form a homogeneous mix, good absorption, and improved anti-stripping properties (Calandra, et al. 2020 & Ismael, et al. 2016). Other studies also documented how there is decreased penetration and increased viscosity when nanosilica is used as a modifier. These enhanced properties are largely dependent in part on the proportion of nanosilica present in the mix (Ashish & Singh 2019; Zani, 2017). Aside from the advantages in mechanical properties, it also provides increased resistance to moisture deterioration, slows the aging process of asphalt, and has a low manufacturing cost. The major drawback associated with its use is the poor compatibility between the organic-based bitumen matrix and the inorganic nanosilica modifier (Calandra, et al. 2020).

Calcium Carbonate nanoparticles

These are relatively cheaper, readily available, and much more stable materials used in asphalt modification. They are largely abundant naturally but can be synthetically manufactured in order to be used as additives for specialized functions. They have versatile applications, but their use is largely dependent on the degree of purity, particle size distribution, and adopted mode of processing (Ezzat, et al.2016). They are largely used in the chemical industry, although construction is another sector that has witnessed a dramatic increase in their usage over the decades. They are used in the manufacture of cement, asphalt, etc. Previous research has documented numerous advantages in using nano $CaCO_3$ as a modifier, some of which include high resistance to thermal rutting at high temperatures, increased tensile strength, enhanced toughness, and good thermal stability when incorporated into the binder (Chong, 2004). Compared to other nanomaterials, they are more easily dispersed in asphalt mix and water stable. They are less sensitive to temperature changes and therefore perform better when subjected to thermal rutting at high temperatures or thermal cracking at low temperatures (Ashish & Singh, 2019; Calandra, et al., 2020; Galooyak, et al., 2010; Ismael, et al., 2016).

Artificial Intelligence

Artificial intelligence (AI) is a collective term that sums up a group of processes that are capable of imitating human cognitive functions like learning, sequence recognition, problem detection, and solving. Using statistical techniques and processes, a machine is able to "train and learn" from available data, which will then be able to perform reasoning at high speeds, getting finer tuned as ıt gets exposed to more data sets. Since its emergence, the use of AI has demonstrated its efficacy at modeling and predicting complex real-life scenarios with greater success than could have been achieved using already available empirical tools. They are better at streamlining or training complex, irregular data sets. But to obtain the best and most reliable results, there should be accurate and readily available data sets as much as possible to help in the calibration of the model. Because of the cumulative errors that will be encountered when using AI, it is best suited for short-term prediction.

In the practical field, AI methods such as Artificial Neural Network (ANN), Gaussian Process Regression (GPR), Bayesian Regression, and Support Vector Regression (SVR) have been adopted and used as they have strong reasoning and explicit knowledge display. The use of ANN has gained popularity over the past years due to its robustness and ability to detect recurring patterns in a given data set. This is evident in the study by Mehdizadeh, et al. (2012), when they used ANN in their predictions of rainfall forecasting and concluded the outcomes were reliable and recommended its use in subsequent rainfall forecasting predictions in other areas. The use of ANN has proven to predict reliable outcomes when sufficient data points and an appropriate network matrix are provided for the training of the model. The use of ANN and Multiple Linear Regression (MLR) has also been jointly employed when accessing the weather forecast because of the complexities involved. It was observed that there was better compliance and similarities in the outcomes when they were used together in the prediction.

Another alternative to ANN is the Least Square Support Vector Machine (LSSVM), which has also proved reliable in making predictions. They have successfully been used in training and predicting non-stationary, non-linear, and much more complex data sets. The efficacy of adopting this model type was demonstrated in the study by Lu and Wang (2018) when it was used in the prediction of monthly precipitation over some selected provinces in China. The outcome of the prediction was promising and favorable and suggested its use in other provinces as well. In recent times, due to the complexity of scenarios and events encountered on a daily basis, a coalition or hybrid of models has been proposed and adopted to help in making better predictions. In the study by Chavhan and Shrivasta (2016), they adopted the use of ANN in their research to estimate the rate of evapotranspiration in the Mahanali reservoir and other climatic conditions and were of the opinion that although the results proved satisfactory, a hybrid with other models would help enhance the predictions. Moghaddamnia, et al. (2015) used ANN techniques to estimate the rate of evaporation from a complex data set. Based on their research, they were able to solve the best input data combination and how the modeling calibrations were affected by the number of data points when using the Gamma test. In the research by Cai, et al. 2019, they proposed using a Multiple Task Gaussian Process (MTGP) in their work. With this proposed method, the limitations and challenges encountered when using the SVR model are greatly minimized. The complexity and flexibility offered by this model make it very suitable for accessing and predicting outcomes when more complex data sets are encountered. It was observed from the results that the accuracy of the predictions had greatly improved. Aside from the use of the ANN and LSSVM methods, the Adoptive Neural Fuzzy Inference System (ANFIS) model is another model relied on because of its robustness, objectivity, and high accuracy predictions. The ANFIS function generates predictions by analyzing the relationship existing between the input and output data sets through a series of training algorithms. The training adapted here ensures that the predicted outcomes are much closer to the actual ones. This model, together with other models such as the Firefly algorithm (FFA), etc., has been instrumental in predicting complex scenarios involving complex data sets, as was the case in the study by Yassen et al. 2018.

Asphalt modification

Asphalt binder modification is an old concept that has generated a lot of curiosity among scientists and engineers. As a result, there have been increasing studies over the past decades and currently to better understand the concepts and mechanisms arising from such modifications so as to apply the knowledge more efficiently to enhance the durability of our road pavements. Modified asphalt binder is specially designed and engineered asphalt where certain chemicals or materials are added to it to enhance its mechanical or engineering properties. These modifiers introduced into the asphalt binders have been observed to produce many desirable properties, and their use is highly recommended when the pavement is exposed to heavy traffic and where the climatic conditions vary significantly between extremely cold and extremely hot (Chen, et al. 2002; Yildirm, 2007; Silva, et al. 2004). Different kinds of modifiers such as polymers (comprising of thermoplastic elastomers, plastomers, thermosetting polymers), chemical modifiers (sulphur, lignin, certain organo-metallic compounds), fillers (hydrated lime, lime, carbon, black, fly ash, and fillers), fibers (cellulose, mineral, plastic, glass, asbestos), hydrocarbons (recycled or rejuvenating oils) and nanoparticles have been identified (Saboo, et al., 2016; Wei, et al., 1996; Yildirm, 2007). A few modifiers are considered satisfactory and widely used in the paving industry because of their superior binder enhancing qualities and economic point of view. Many factors are known to affect modified asphalt. One of the factors affecting the properties and behavior of modified asphalt is the chemical composition of the neat binder. Although crude oil is a complex mixture of hydrocarbons, and although asphalt binders are basically composed of similar constituent elements, the percentages of these constituent elements can vary greatly depending on the source of the crude oil. The elements in it, which include oxygen, nitrogen, sulfur, iron, vanadium, nickel, magnesium, calcium, etc., come in different percentages. These can broadly be categorized as saturates (S), aromatics (A), resins (R) and asphaltenes (A), commonly referred to as the SARA fractions (Behnood, et al. 2018). The polarity, or molecular weight, directly affects how the binder interacts with other chemicals, thereby influencing the overall properties of the binder. Other factors influencing the properties of modified asphalt include the internal structure of the asphalt and the internal structure of the modifier (polymer and nanoparticles). So generally, the compatibility of these modifiers and the binders is closely linked to the chemical composition of the virgin bitumen, the molecular structure of the modifier, particle size, polarity, modifier type, preparation conditions, and modification process adopted (Behnood, et al. 2018; Partl, et al. 2004; Silva, et al. 2004; Yang, et al. 2014; You, 2011). Through the modification of these asphalt binders, it has been observed that there is improvement in some asphalt properties such as ductility, elasticity, rigidity, storage stability, among others. Currently, there has been increased research and application of nanotechnology in the road construction industry over the last decade. This has resulted in a potential antidote to mitigate the defects in asphalt such as rutting, cracking, etc., by tremendously enhancing the durability and performance of paving asphalt. Many different modifiers exist in the production of modified asphalt concrete, but for a modifier to be considered suitable and adopted in real-life usage, there are certain criteria that it needs to fulfill. Among the properties desired is the ability of the modifier to adequately improve the rheological properties of the binder so that the pavement can sufficiently resist the imposed stresses from traffic or climatic conditions (i.e., precipitation and temperature) that could have led to failure or deterioration of the pavement (Behnood, et al. 2018; Galooyak, et al., 2010; Ghile, 2006). Apparently, a good modifier should also have the following characteristics: being readily available in sufficient quantities, being cost-effective, easily blending with bitumen, improving resistance to flow at high road temperatures without making the bitumen too viscous at mixing and laying temperatures or too stiff or brittle at lower road temperatures, resulting in improved binder and aggregate cohesion or adhesion properties, and being physically and chemically stable during the application process. It has become evident from past studies that the physical, mechanical, and rheological properties of modified asphalt binders are largely influenced by many factors and conditions. The viscosity of the modified binder is influenced by the homogeneity of the mixture from the mixing process. It is therefore important that in order to achieve the intended and desired properties, certain critical factors during the mixing process, such as mixing duration, temperature, and speed, are given much attention. Factors such as the type of modifier, the percentage (%) content of modifier added to the mixture, the chemical makeup of the binder, and mixing conditions such as mixing times, mixing temperature, and mixing procedure all have an impact on homogeneity. The specific temperature, speed, and duration will largely depend on the specific binder and the modifier. High temperatures during the mixing process help in the dispersion of the modifier in the binder, but extremely high temperatures have the tendency to create undesired thermal effects. To obtain an ideal mix, it is important to operate at the lowest possible mixing temperature for the minimum duration permissible. Due to the difference in the molecular build-up of the binder and the modifier, mixing is a difficult task that involves shearing the modifier in order to break it. The chemical reaction when an asphalt binder and a modifier are mixed leads to three possible outcomes. First, a heterogeneous mixture is formed due to the molecular weight differences, leading to the formation of phases between the mixture, which is not recommended. Second, there could be the formation of a homogenous mixture, but the difference in their molecular weight and arrangement leads to undesirable qualities such as increased viscosity, making pouring and placing of these asphalt mixtures unrealistic. (Xiao, et al., 2014). Lastly, the formation of finely and fitly interlocking phases of the mixture leads to variations in the chemical structure possessing desirable mechanical properties (Da Silva, et al.2004). Previous studies indicate that modified binders have increased flexibility and resistance to penetration at higher temperatures when compared with unmodified binders. There was also increased elasticity exhibited by the asphalt mixture, thereby making it more flexible under stress, which in effect allowed the pavement to withstand cracking at low temperatures (Yildirim, 2007; Becker, et al., 2001).

Because of the complexity with which most compounds exhibit when mixed together, it has become necessary to analyze the mechanism and dynamism occurring in the mixture so that the necessary modifications can be made to ensure that the asphalt mixture performs at its highest expected capabilities. It is worth noting that the storage stability of modified binder is directly linked to the compatibility between the asphalt binder and the modifier (Ren, et al.2020). Phase separation is a common phenomenon that occurs in modified binders, and this comes about because some of the constituents of the asphalt binder, that is, asphaltenes, have heavier densities, making them sink to the bottom while the modifier gets dispersed on top of the asphaltenes. During this stage, the mixture can have stability and separation problems, which may cause the mixture to lose most of the benefits that come with bitumen modification. Therefore, changes encountered during the storage phase stage can have serious repercussions on the overall performance of the mixture. Rutting in asphalt pavement is considered to be one of the major distresses encountered by the pavement during its service life, so numerous studies have been carried out over the years to find ways to mitigate this defect in asphalt concrete. The research by Zhu, et al. (2014), Xiao, et al. (2014), and Polacco, et al. (2008) indicated that the binder properties at high temperatures were greatly influenced by the added polymer modifiers. At high temperatures, there was a significant increase in the complex modulus G* at high temperatures, which showed an increased resistance to rutting, and at lower temperatures, there was an increased resistance to thermal cracks. This indicates that when incorporated into the binder, defects that relate to low temperature cracking and permanent deformation of the pavement as a result of rutting experienced during elevated temperatures are greatly controlled. In the study by Becker et al. (2001), they theorized that the addition of SBR has conferred numerous advantages upon its introduction in the pavement industry. There was increased ductility exhibited by the asphalt mixture, thereby making it more flexible under stress, which in effect accounted in part for the pavement's ability to withstand cracking at low temperatures and was highly recommended for use in cold regions where thermal cracking is a major problem. In the research where Asmael et al. (2018) undertook a performance evaluation of polymer modified asphalt binder, they concluded that the performance of the modified binders was enhanced regarding their resistance to thermal rutting at high temperatures when an optimum amount of the modifier was used. This indicates that when these modifiers are incorporated into the binder, defects such as rutting deformation experienced during elevated temperatures are greatly minimized. This view was shared by Mubaraki, et al. (2016) when they evaluated and characterized the properties of modified asphalt concrete at high temperatures and observed that the binder properties at high temperatures were greatly influenced by the added modifiers ASA and Al_2O_3 nanoparticles (Ali, et al., 2016; Mubaraki, et al., 2016). There was good compatibility during mixing and storage, greater resistance to rutting at elevated temperatures, and increased creep recovery in the asphalt cement. They therefore concluded that at an optimum content of 5% of the modifier, defects associated with asphalt cements at high temperatures are greatly minimized. Jahromi et al. (2009) concluded in their quest to study the effects of nanoclay on the rheological properties of bitumen binder that nanoclay when used as a modifier in optimum quantity can significantly improve the stability, tensile strength, and temperature susceptibility of the modified binders, similar to the ideas shared by Mahdi et al. (2013) and Ali et al. (2016). Similarly, the effects of nanoparticles on the rutting behavior of hot mix asphalt studied by Nejad, et al. (2014) came to the conclusion that there was a recorded increase in the resistance to rutting at high temperatures when the binder was incorporated with an optimum amount of nanoparticles. This conclusion was supported by the experimental work of Bagshaw (2018) and Zangera (2019). Although the field test conducted by Blankenship, et al. (1988) using different polymers as modifiers in the base asphalt binder gave slightly different results from the laboratory testing, it was still evident from the results obtained that the use of polymers in the binders recorded significantly enhanced properties when compared with the unmodified binder. It was observed that there was greater resistance to rutting at high temperatures and increased creep recovery in the asphalt cement. This led them to conclude that at optimum modifier content, asphalt defects associated with asphalt cements at high temperatures are greatly minimized. Similarly, in the study by Chong, (2004), he investigated the effects of nanoparticles on the rutting behavior of asphalt concrete and concluded that there was increased resistance to rutting at high temperatures when the binder was incorporated with an optimum amount of nanoparticles. There was a new twist in the study by Xiao, et al. (2011) in their experiment to determine the long-term aging influence on the rheological characteristics of asphalt binders containing carbon nanoparticles, which indicated that the addition of nanoparticles does not yield any appreciable value in shear modulus G*, deflection, and stiffness. They therefore concluded that at nano percentages of 0.5–1.5%, there was no appreciable improvement in the binder qualities and that the binder source and grade, rather than the nanoparticles, were responsible for determining the rheological mixture properties.

From these studies, it is evident that both polymers and nanoparticles used as modifiers in asphalt binders play crucial roles in the overall properties and performance of any asphalt pavement. Since the cost associated with asphalt modification is relatively high, its adoption for use on a commercial scale is only laudable and profitable if the quantity of the modifier, polymer, or nanoparticles needed in the modification process to obtain the desired outcome is relatively small (Xiao, et al. 2014). These modifiers have enhanced the properties, such as providing greater elasticity, increasing the softening point temperature, lowering the penetration, providing optimum viscosity to facilitate easy workability, and most importantly, providing complex modulus values sufficiently low at medium-low temperatures to resist thermal cracking and adequately high at elevated temperatures to resist permanent deformation from rutting.

CHAPTER III

Methodology

This chapter presented and followed scientific methods of research by describing the test samples and the standard testing procedures followed in the sample preparation and measurement.

Materials

The unmodified asphalt binder used in this study had a 60/70 penetration grade as a reference, and two binders were modified with polymers, namely; 5% ENR, 5% ASA, and the other two binders were modified with nanoparticles, namely; 5% Al_2O_3 and 5% $CaCO_3$. The modified asphalt binders were produced in the laboratory using polymers and nanoparticles. The ASA polymer, nano Al_2O_3, and $CaCO_3$ were in powder form, while the ENR containing 53% epoxidation was subjected to sieve analysis, passing a 2.36 mm mesh sieve, and was added and blended with the asphalt binder. Table 1 shows the physical properties of unmodified and modified asphalt binders.

Table 1

The physical properties of the unmodified and modified asphalt binders

Material	Properties	Unit	Value
Asphalt 60/70	Specific gravity	-	1.03
	Penetration @ 25 °C	0.1 mm	70
	Softening point	°C	47
	Viscosity @ 135 °C	(Pa s)	≤ 3
	Ductility @ 25 °C	cm	≤100
	Form	-	Powder

Table 1

The physical properties of the unmodified and modified asphalt binders (continued)

Material	**Properties**	**Unit**	**Value**
ENR	Size	mm	2.36
	Specific Gravity	-	0.94
	Form	-	granular
ASA	Size	mm	2
	Form	-	Powder
Al_2O_3	Size	nm	13
	Form	-	Powder
CaCO3	Size	nm	40
	Form	-	Powder

Samples preparation

The samples of the modifiers ASA, Al_2O_3, and $CaCO_3$ were prepared using the melt method. The 5% of modifiers were added and blended with the base asphalt binder using a Silverson high-shear mixer at a speed of 5000 rpm and a temperature of 170 °C (1 °C) for 1.5 hours to produce homogenous mixtures. For 1 hour, 5% ENR in granular form was prepared using a high-shear mixer at a lower temperature of 160 1 °C and a higher mixer speed of nearly 8000 rpm.

Testing Procedures; Conventional binder test (Physical properties)

Many conventional tests were performed according to ASTM standards to determine the physical properties such as penetration, softening point, and viscosity of the unmodified and modified asphalt samples. The penetration test was performed using a penetrometer, and this gave an empirical measurement of the consistency of the test sample. Here, the test samples were adequately heated to pouring consistency, thoroughly stirred, and subsequently poured into containers at a temperature of 25 °C

0.5 °C (ASTM D5). Higher penetration values obtained mean the sample has a softer consistency and vice versa. The softening point test was performed using the Ring and Ball apparatus, where two horizontal brass rings containing the asphalt disks were prepared, with each disk supporting a standard steel ball. In a controlled water bath, the sample was gently heated at a controlled rate of 5°C per minute. The softening point was determined to be the average temperature when the enclosed steel balls on top of the asphalt disks descend to a lower metal place, which is at a distance of 25 mm (ASTM D36). A sample having a higher softening point value will be preferred in hot climates because of its lower temperature susceptibility. The viscosity test was carried out to ascertain the fluid nature of the sample and its resistance to flow. The Brookfield rotational viscometer was used for the testing to determine the viscosity of the unmodified and modified binder samples. The Superpave test procedures and parameters were followed where a spindle number of 27 was used at a controlled speed of 20 rpm. At each test temperature, three (3) readings were taken and the mean of these temperatures was noted. The test samples were performed under temperatures of 135°C and 165°C (ASTM D4402).

The sample to be tested was poured into an aluminium foil having a diameter of 30mm and an overall length of 300mm. The sample was securely covered and allowed to stand vertically for 48 hours at a temperature of 163 5°C in an unattended oven. It is then cooled at room temperature and cut horizontally into three identical sections. The upper and bottom sections of the cooled sample were placed in separate beakers and their softening points were tested. If the difference in temperature between the upper and bottom sections was 2.5 °C or less, then the binder would exhibit good storage stability. In contrast, the sample could be considered unstable during storage if the variation in temperature between the upper and bottom sections exceeds 2.5 °C (Zhang, et al. 2011).

Rheological Properties Test

A dynamic shear rheometer (DSR) was used to describe the viscous and elastic behavior of asphalt cement at intermediate to high temperatures by measuring the complex shear modulus (G^*) and phase angle (δ). A frequency sweep test was conducted to ascertain the rheological properties of the asphalt cement samples. This was carried out using the Rheometer HAAKE Rheo Stress 600, which was operated at frequencies of 1 to 100 rad/s (0.159–15 Hz) while the temperature ranged from 25 ˚C to 75 ˚C.

Gaussian Process Regression (GPR)

Gaussian Process Regression (GPR) is a unique class of machine learning algorithm that uses nonparametric technique that can rely on a few input parameters to make complex statistical modelling and predictions. The popularity of using GPR has gained ground in recent years in solving complex engineering challenges (Rasmussen, 2004) because of the flexibility and ease with which few input parameters are able to be modelled to make predictions. This unique feature, where even with little data, a wide range of supervised learning problems can be solved, makes its adoption and usage laudable. A Gaussian Process is usually characterized by having random sets of variables where, at any given point, there is an accompanying set of multivariate Gaussian distribution.The general expression of the GPR is of the form

$$y_i = f(x_i) + \varepsilon \quad (1)$$

Where $f(x_i)$ signifies arbitrary variables that links the input data to the predicted output, ε represents regression error that has similarly distributed function having the mean figure of 0 and variance of σ^2.

When considering a function having unobserved pair (x^*, f^*) where f is the response and x is the explanatory parameters can be achieved from:

$$\begin{bmatrix} f \\ f^* \end{bmatrix} \sim N_{n+1}\left(0, \begin{bmatrix} K(X,X) & k(X,x^*) \\ k(x^*,X) & k(x^*,x^*) \end{bmatrix}\right) \quad (2)$$

In equation 2, $K(X, X)$ represents the matrix of covariances (n x n) for all values in the calibration set, k (X, x*) symbolises the vector of covariances ($n \times 1$) amidst the point

x^* and calibration set *k(x*, x*)* is the variance at point x^*. The mean *(f)* in a classic regression, is derived from f which is then integrated to f^*:

$$P(f * \mid x *, X, f) = N \mid (k(x *, X)K(X,X)^{-1}f, k(x *, x *) - k(x *, X)K(X,X)^{-1}k(X, x *)) \quad (3)$$

The equation (3) features X and f by enhancing the joint probability of f^* conditional on x^* to obtain the f^*.

When using data that is noisy, it should be supplemented by a model for the observation error. Hence, Equation (4) is converted into:

$$\begin{bmatrix} f \\ f^* \end{bmatrix} \mathrm{N}_{n+1}\left(0, \begin{bmatrix} K(X,X) + \sigma^2 \mathrm{I} & k(X,x^*) \\ k(x^*,X) & k(x^*,x^*) \end{bmatrix}\right) \quad (4)$$

Consequently, the conditional likelihood and the variance change to

$$f(x^*,) = k\,(x^*,\ X)\,(K\,(X,X) + \sigma^2 I)^{-1} f \quad (5)$$

&

$$Cov\,(f(x^*)) = k\,(x^*,x^*) - k\,(x^*,X)\,(K\,(X,X) + \sigma^2 I) - k\,(x,x^*) \quad (6)$$

with I indicating the identity matrix and σ^2 represents the variance of the measured error (Bonakdari et al., 2019).

Data pre-processing and performance evaluation

In a real-world scenario, it is likely that sizable quantum of the datasets used in machine learning are prone to inconsistencies, omissions and noise due to the heterogeneous source. Data preprocessing is therefore a prerequisite process because it ensures the dataset is more accurate as redundancies as a result of human factors or other factors are eliminated. This stage also enables us to fill missing data if the need be and finally, it makes the reading and interpretation of the observations much easier. In this study, the data preprocessing steps adopted were data cleaning, data integration, data transformation, data reduction and data cleaning. In the normalization process, the numerical entities were scaled up or scaled down between the values of 0 and 1. By adopting this process, there was the elimination of high-valued data sets from overshadowing or domineering the low-valued data points and making them look insignificant (Umar et al., 2021). This step was necessary because the ranges of the dataset were different. The min-max scaling formula adopted in the normalization process was from equation 7 below;

$$Leq_{norm} = \frac{Leq - Leq_{min}}{Leq_{max} - Leq_{min}} \tag{7}$$

Where Leq, Leq_{max}, and Leq_{min} represent the values of observed, maximum and minimum noise levels, respectively, while Leq_{norm}indicates the normalized noise.

In any machine learning, it is important to evaluate the accuracy of the adopted model to determine how well it will perform in its predictions. The metrics that will be used in evaluating the model in this study to ascertain how the predicted outcomes deviates from the actual target are root mean square error (RMSE), determination coefficient (R^2), and the mean absolute error (MAE). R^2 is scale-free and this represents how well the predictions in a model fit the original data set. The R^2 values lie between 0 and 1 so the closer the attained value nears 1 the better the results. The RMSE measured the standard deviation of residuals and falls between zero and + with the best model having a value of zero (Nourani and Fard-Sayyah 2012). Residuals / errors are the differences between the predicted values and the actual values (Umar et al., 2021). The MAE represents the average of the absolute difference occurring between the original and forecasted data values. Similar to the use of RMSE, MAE measures the average of the errors existing in a dataset with the best model will have a value of 0.

The performance of the model was evaluated using the metrics;

$$R2 = 1 - \frac{\sum_{i=1}^{n} \left(N_{obs_i} - N_{pre_i}\right)^2}{\sum_{i=1}^{n} \left(N_{obs_i} - \overline{N_{obs_i}}\right)^2} \tag{8}$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} \left(N_{obs_i} - N_{pre_i}\right)^2}{n}} \tag{9}$$

$$\text{MAE} = \frac{\sum_{i=1}^{n} \left| X_{obs_i} - X_{pre_i} \right|}{n} \tag{10}$$

where n represents the number of observations, $\overline{N}_{obs}$ is the average value of observed values, N_{obs} is the observed value, and N_{pre} represents the value of the predicted

CHAPTER IV

Results and discussions

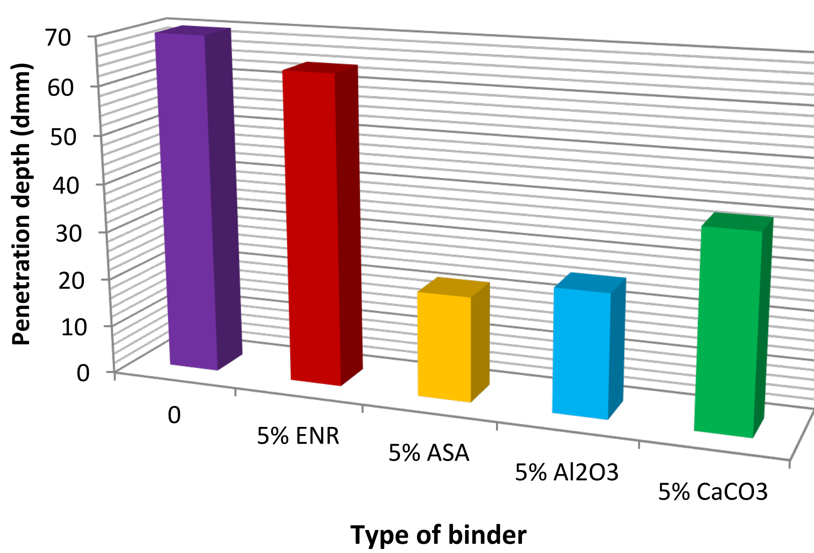
Effect of modifier on physical properties of binders

Penetration

Figure 4.1 depicts the penetration values of the different test binders. It was noted that the unmodified binder had the highest penetration value of 70 dmm. The binder having 5% ENR recorded the second highest value of 64dmm, followed by 5% $CaCO_3$ and then 5% Al_2O_3 binders with values of 40dmm and 25.45dmm, respectively. The binder to record the least penetration value or the highest penetration resistance was the binder with 5% ASA. This greater resistance exhibited by the binder could be attributed to particle size distribution and the stiffness of the binder. This situation has the added advantage of making the mixture more resilient to high temperature deformations

Figure 1

Penetration test of unmodified and modified binders

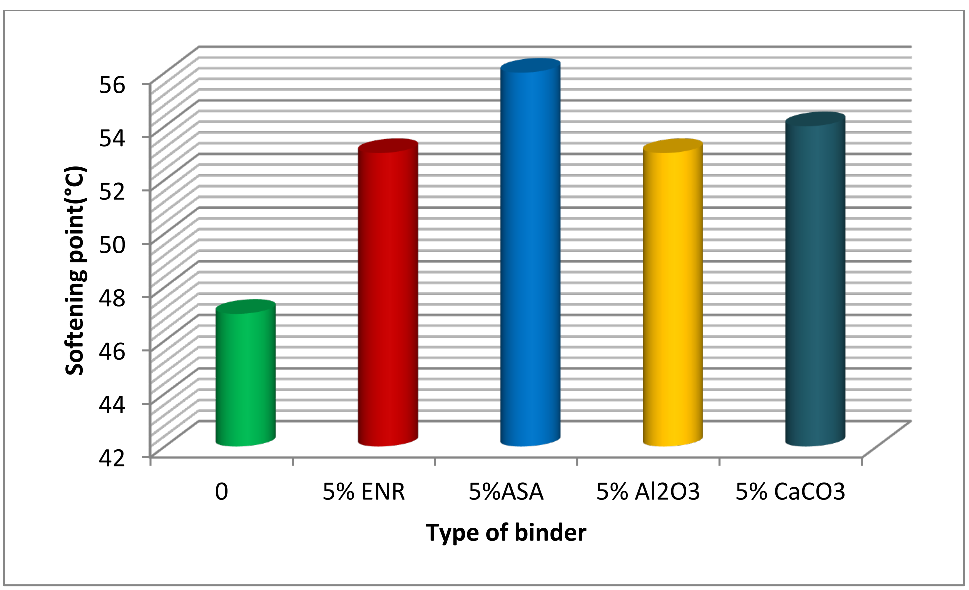


Softening Point

Softening point is an undertaking primarily to determine the temperature at which a phase change will occur in the binder under standardized conditions. A high softening point indicates low temperature susceptibility and vice versa. In Figure 4.2 below, it was observed that the base binder had the least softening point temperature of 47°C. The modified binders had relatively higher softening points compared to the base binder. As can be seen, 5% ASA recorded the highest softening point temperature of 56°C. The modified binders, 5% ASA, 5% ENR, and 5% Al_2O_3 both recorded equal values of 53°C, while 5% $CaCO_3$ had the second highest softening point temperature of 54°C. From these results, the modified binders will generally have increased resistance to rutting, with the 5% ASA binder having the greatest tendency to resist deformation at intermediate to high temperatures, which is low temperature susceptibility.

Figure 2

Softening Point of unmodified and modified binders

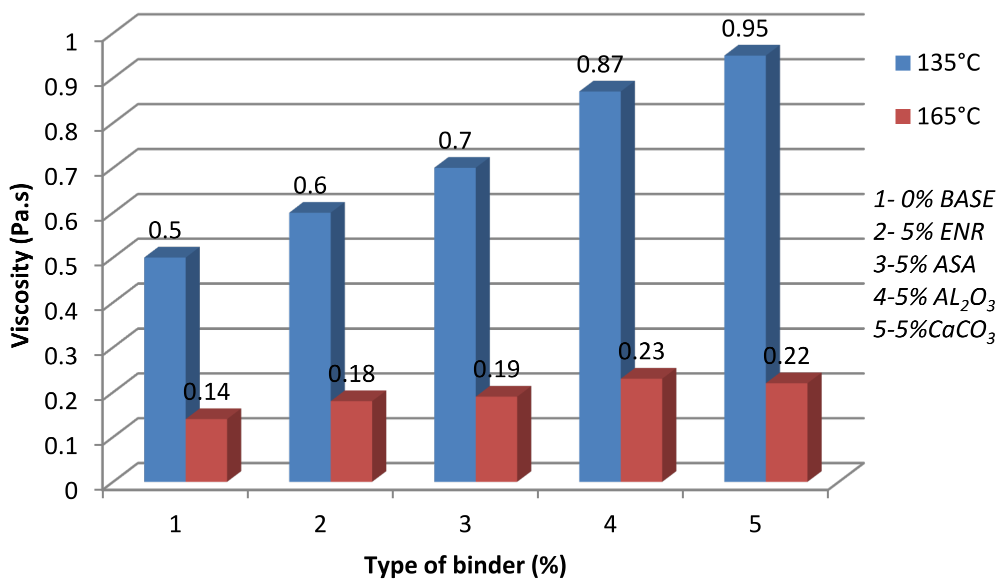


Viscosity

Viscosity in a bituminous binder can be defined as the resistance to flow in a binder. After carefully examining the outcomes from these two studies (Yao, 2012 & Zani, 2017) and considering the graph presented in Figure 4.3, as expected in all binders, there was a recorded decline in viscosity with increasing temperature as the mixture slowly moves from the solid to the liquid state. It was observed that at a predetermined temperature on the viscosity/temperature scale, the viscosity of the modified binders was higher compared to the unmodified binder for most parts of the experiment, indicating that the modified binders had better performance at high temperatures. This in effect gives an indication of how workable the binder will perform. The greater the viscosity of the mixture, the greater the difficulty in its workability properties

Figure 3

Viscosities of Unmodified and Modified Asphalt Binders

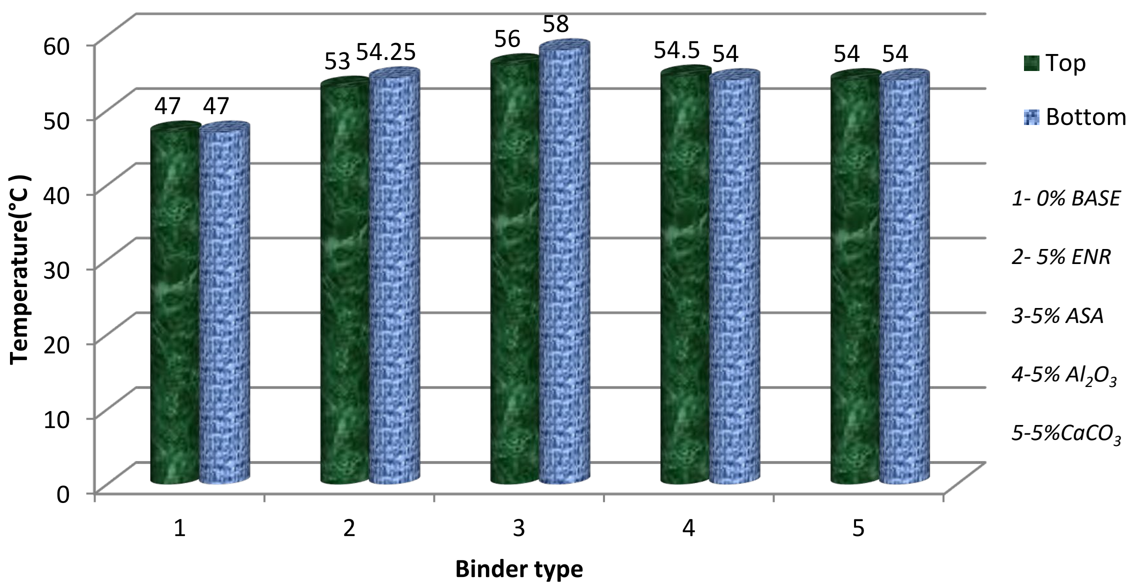


Storage Stability

It is expected that a binder will have good storage stability properties if the difference in the softening point temperatures between the lower and upper test sections is equal to or less than 2.5 °C. In Figure 4.4, it was observed that all the binders used in the test had a temperature difference of less than 2.5 °C. It is therefore evident that all the binders will exhibit good compatibility, good workability properties and stable storage during high temperature.

Figure 4

Storage Stability of unmodified and modified binders



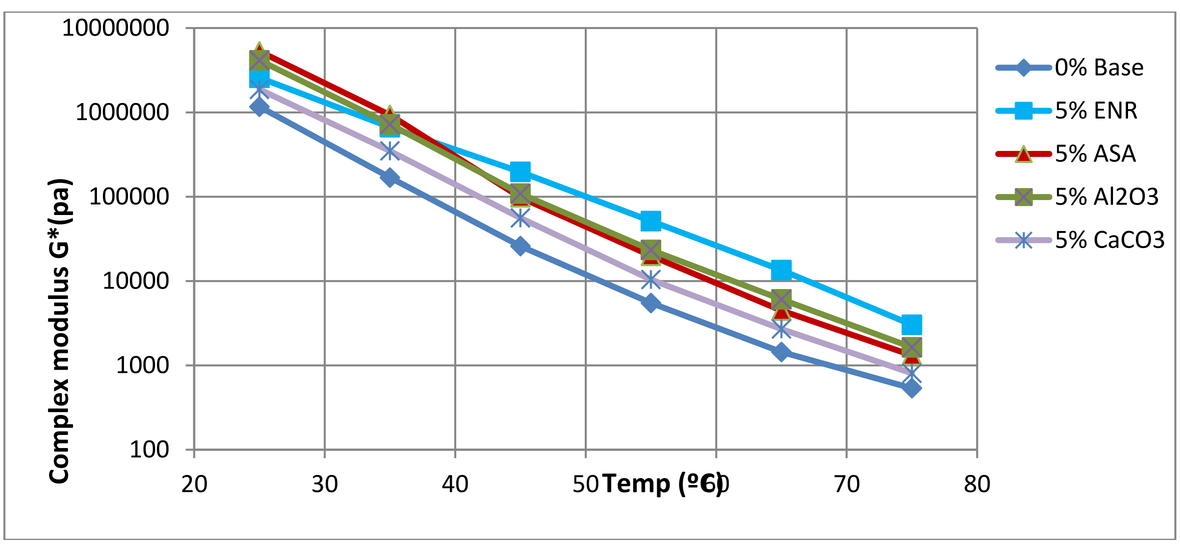
Effect of modifiers on rheological properties of binders

Isochronal Plot

The isochronal plot can be used to determine the viscoelastic properties of the different binders when evaluated over a set of temperature ranges at a specific frequency.The isochronal plots were created from Fig 4.5 using the complex modulus G* and temperature (°C) at a reference frequency of 1.592Hz. As expected, there was a general decline in the G* value for all the corresponding binders, both the neat and the modified binder, with the increment of temperature. Apparently, all the G* values of modified binders superseded those of the neat binder. In incremental order, the binder containing 5% $CaCO_3$ performed better than the neat binder, followed by the binder with 5% ASA, 5% Al_2O_3 and then finally the highest with 5% ENR. The 5% ENR having the highest G* values indicates that the binder has the greatest tendency to resist applied stresses acting on it before failure. This in effect means that when used in the construction of asphalt pavements, they will exhibit better rutting resistance properties compared to other binders

Figure 5

Isochronal Plot of Complex Modulus for Unmodified and Modified Binders

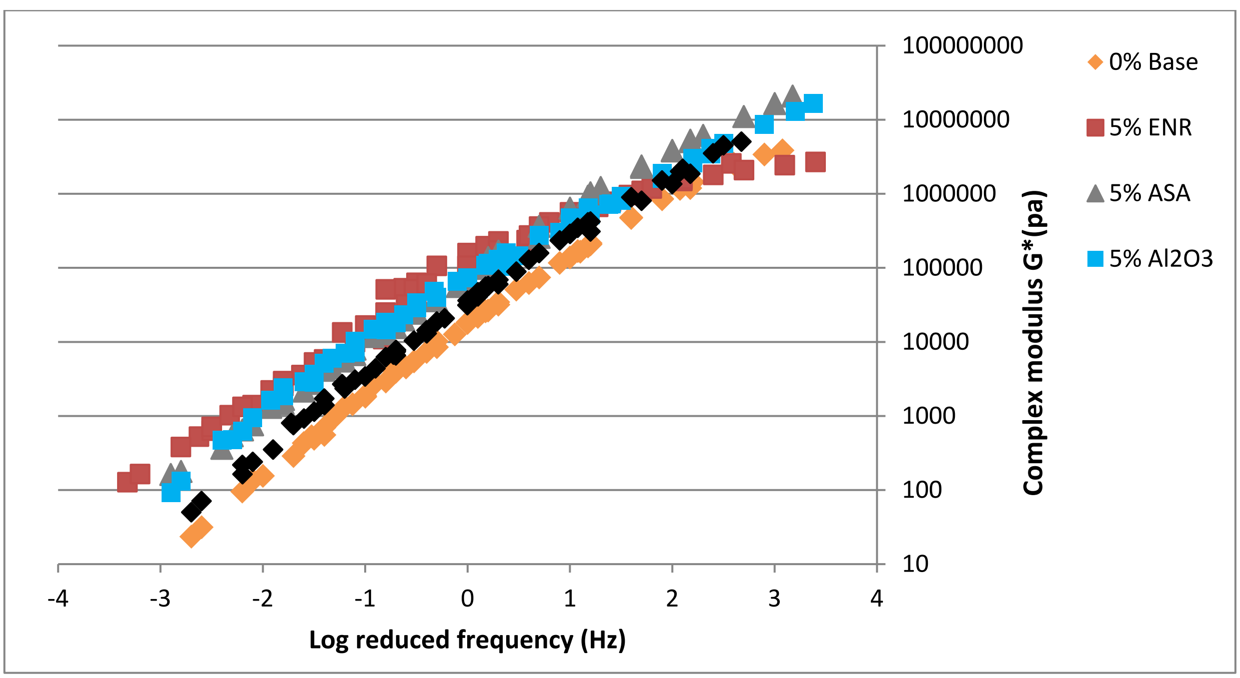


Rheological Master Curve

The master curves for the different binders were constructed to establish the relationship that exists between the complex modulus and the reduced frequencies under multiple temperatures and time. To construct the master curve, a reference temperature is adopted while making adjustments to other temperatures so that a single continuous smooth curve is achieved. This curve enables us to predict the binder stiffness and its properties at any given temperature. The master curves for the base and the different modified asphalt binders are shown in Figure 4.6. It can be observed that the base binder had the lowest complex modulus to reduced log ratio. In descending order, the 5% $CaCO_3$ performed better but was less to the base in resisting stresses than the 5% Al_2O_3 and 5% ASA, respectively. The binder with the greatest tendency to resist permanent deformation was that of 5% ENR.

Figure 6

Complex Modulus Master Curve for Base Binder and Modified Binders

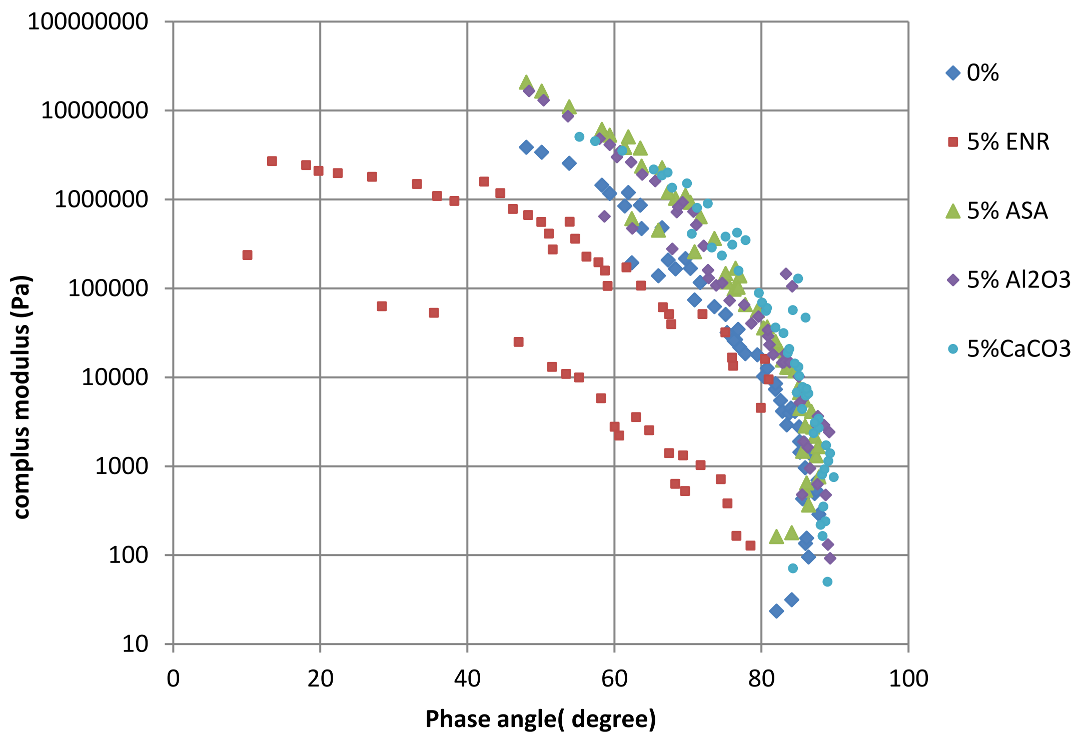


Black diagram

A black diagram was constructed using the complex modulus obtained against phase angle to determine the viscoelastic property of the different binders. This is presented on a single plot without implementing any shifting factor. Figure 4.7 shows that although all the binders did offer some degree of elasticity and were able to resist rutting to some extent, 5% ENR had the highest G* at low phase angle compared to the other binders, indicating its better resistance to rutting and deformation

Figure 7

Black Diagram for the Neat and Modified Binders

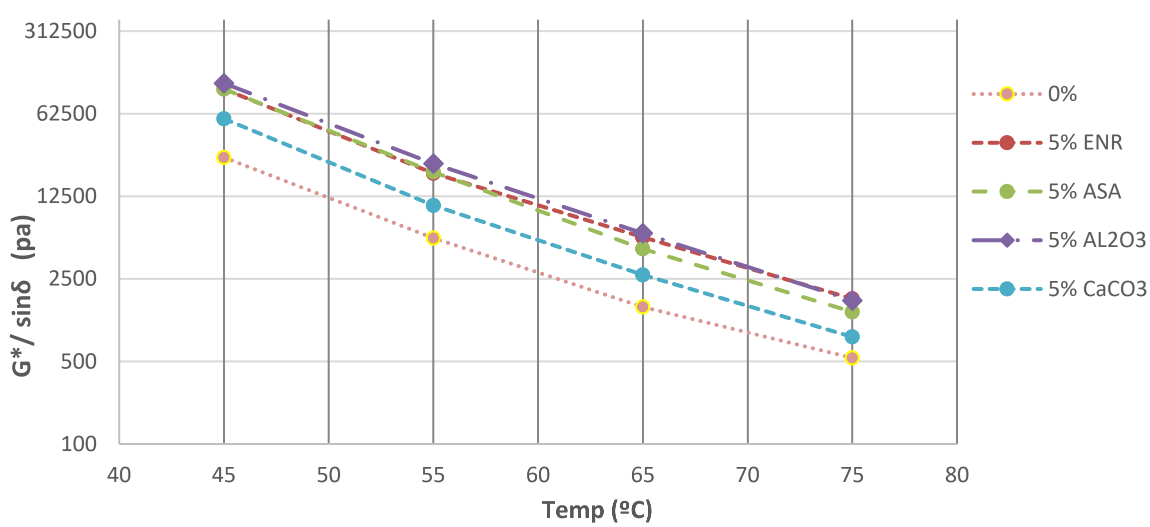


Rutting Parameter

To determine the rutting attributes of the unmodified and modified asphalt binders, the $G^*/\sin(\delta)$ was plotted at temperatures of 45 °C, 55 °C, 65 °C, and 75 °C as specified by the Strategic Highway Research Program (SHRP). It is observed from Figure 4.8 that the lowest value of $G^*/\sin(\delta)$ was recorded by the neat binder. This was followed by 5% $CaCO_3$. Although the $G^*/\sin(\delta)$ values recorded for 5% ENR, 5% ASA, and 5% Al_2O_3 were closely matched, 5% Al_2O_3 had the highest value, closely followed by 5% ENR and 5% ASA in that order. From these values, it is evident that the binder containing 5% Al_2O_3 has the greatest ability to resist permanent deformation and has the greatest toughness at high temperatures. It could be observed from the plot that all modified binders had a $G^*/\sin(\delta)$ exceeding 1000 Pascals at 70°C. Similar outcomes from these results had earlier been concluded by Ali et al. 2016. Moreover, the high values obtained for the complex shear modulus of the nano-modified binders indicated the ability of the binder to take up large stresses by dissipating applied forces acting upon it during high and intermediate temperatures, thereby providing good rutting resistance and fatigue resistance.

Figure 8

Effect of temperature on rutting parameter of base and modified asphalt binders

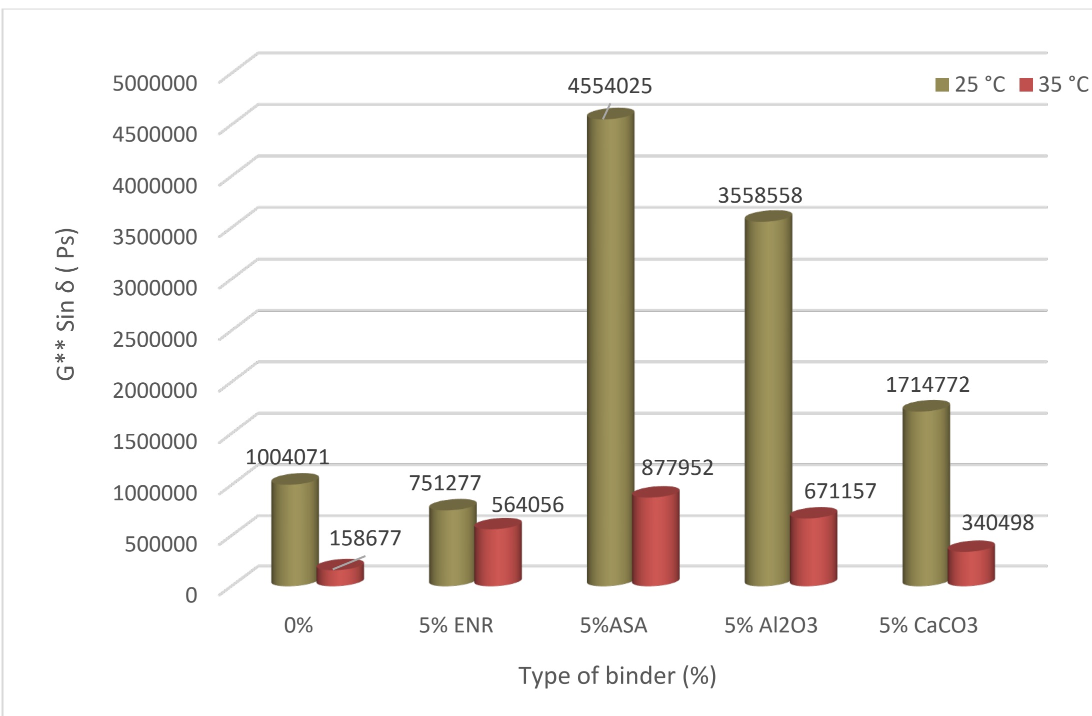


Fatigue Parameter

In determining the fatigue parameter of bitumen at intermediate temperatures, the Superpave stipulates a maximum value of 500 kPa and this is described by the formula G*sin (δ). A frequency sweep test was performed at test temperatures of 25°C and 35°C under a constant loading frequency of 1.592Hz (10 rad). At a temperature of 25°C, all binders, including the base binder, have values greater than the required minimum stipulated by Superpave. This demonstrates the better performance of the modifiers to resist fatigue at intermediate temperatures. This conclusion was also proved by Chen & Zhang (2012). But at 35°C, the neat binder and the 5% $CaCO_3$ failed to meet the required minimum.

Figure 9

Effect of Temperature on Fatigue Parameter of Base and Modified Asphalt Binders

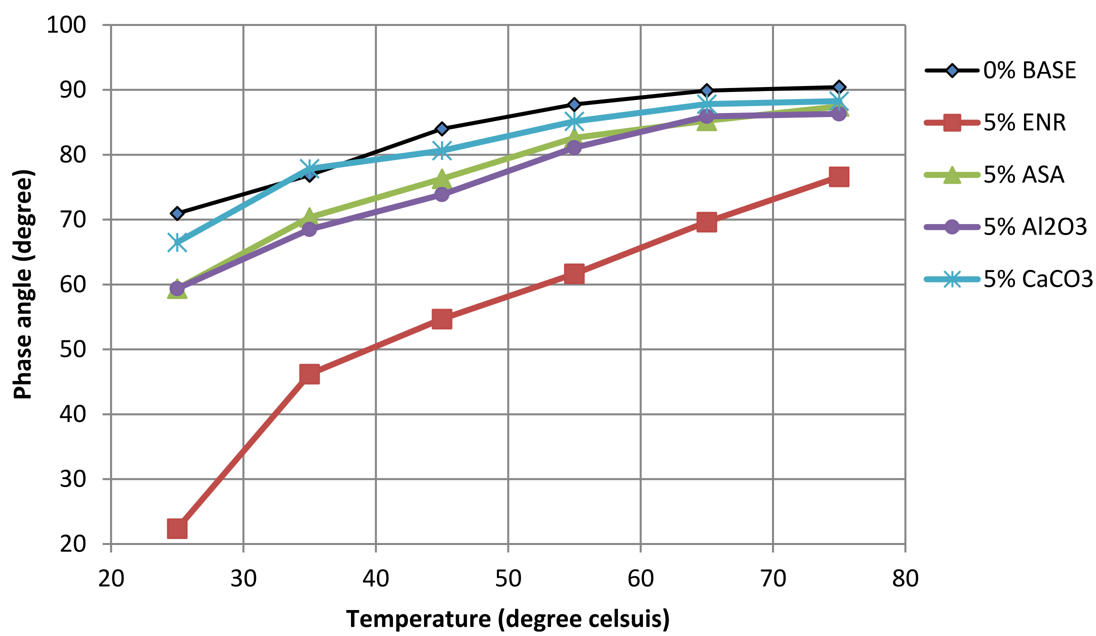


Phase angle

The phase angle is the time lag between the applied stress and the corresponding strain. This curve is particularly helpful in understanding the viscoelastic properties of the binder material and also indicates the mechanical loss. In a perfectly elastic body, there is no time lag, which is zero, when there is an applied load, but a highly viscous binder will have a large phase angle value approaching 90ºC. As a general rule, the smaller the value of the phase angle obtained, the better it will be elastic. Figure 4.10 shows the pictorial representation of phase angle for a viscoelastic binder with no modifier and four other modified binders containing 5% ENR, 5% ASA, 5% Al_2O_3 and 5% $CaCO_3$. It was observed that the base binder had the greatest time lag when subjected to stress, indicating its low elasticity. Although the different binders had some degree of elasticity when subjected to stresses, the binder with 5% ENR had the lowest phase angle values, which is an indication that it is the most elastic binder among the compared binders.

Figure 10

Isochronal Plots of Phase Angle at 1.5 Hz for the Base and Modified Binders

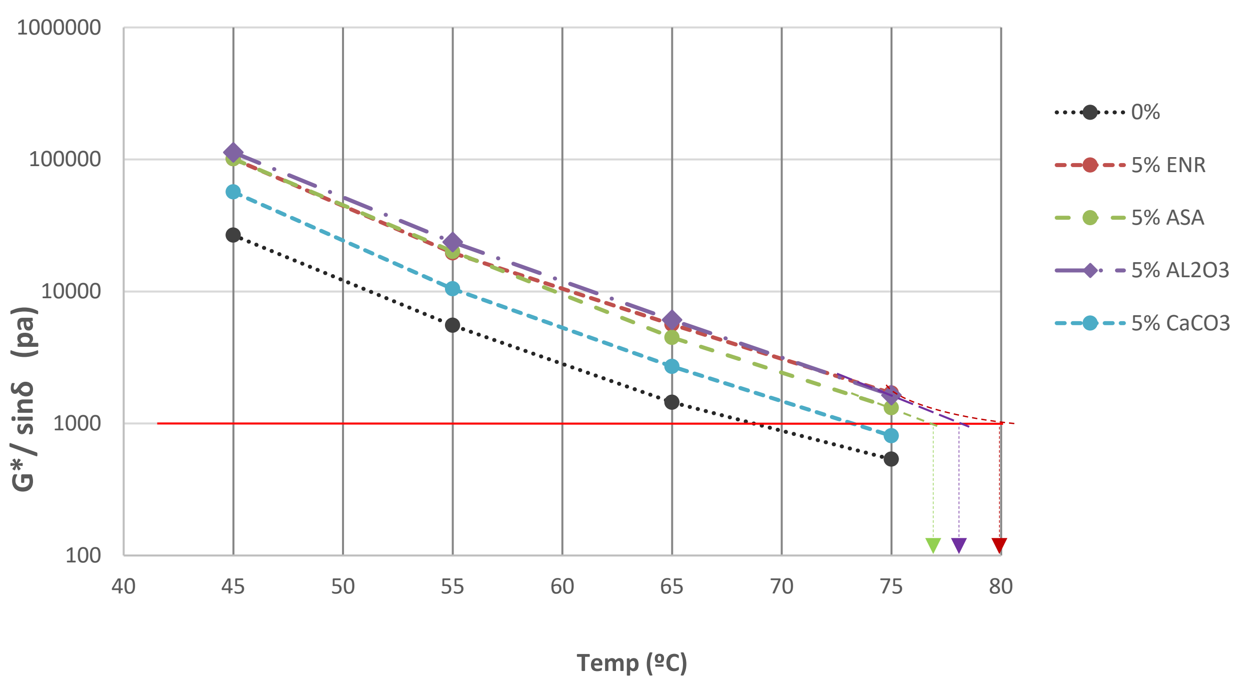


Failure temperature

According to the Superpave specifications, the failure temperature of an asphalt mixture is the point where the value of $G^*/\sin(\delta)$ falls below 1000Pa. This is the widely used criteria adopted in determining the performance grade of asphalt binders (Xiao et al., 2014). In Figure 4.11, the results indicated that the lowest failure temperatures were recorded by the base binder and 5% $CaCO_3$, with temperatures of 69 °C and 74 °C, respectively, which indicates that they are more sensitive to temperature. The other modified binders, namely 5% ASA, 5% Al_2O_3 and 5% ENR, had higher failure temperatures of 77 °C, 78 °C and 80 °C, respectively, when compared to the base asphalt.

Figure 11

Failure temperatures of unmodified and modified binders



Regression Analysis:

The Matlab toolbox, which is a programming platform designed to analyze data, develop algorithms, create models, and design systems, was used in this study. To obtain the optimum model structure, Bayesian optimization search was used. Table 2 shows the regression summary obtained in the analysis. The model is described as a good fit if the coefficient of determination R2 is close to 1 (100%). From the study, *R2* had a good fit of 98% for the unmodified binder, 97% for 5% $CaCO_3$, 85% for 5% ASA, 81% for ENR, and 60% for 5% Al_2O_3. The RMSE is good if the value is close to zero and, as was observed, the corresponding values were 0.028, 0.037, 0.074, 0.113, and 0.124, representing unmodified binder, 5% $CaCO_3$, 5% ASA, 5% ENR, and 5% Al_2O_3 respectively. The scatter plots from Figure 4.12 to Figure 4.16 show the values are compacted along the bisector, indicating closeness between the observed and predicted values in the training and testing phase. This therefore means that the parameters of temperature, frequency, and phase angle used in the regression model are better in predicting the general asphalt cement properties

Table 2 Modelling Results

	RMSE	***R2***	***MAE***
Model 1 *(0%),*	0.02827	0.98	0.0123
Model 2 *(5% ENR)*	0.11379	0.81	0.0536
Model 3 *(5% ASA)*	0.07415	0.85	0.0209
Model 4 *(5% Al_2O_3)*	0.12425	0.60	0.0344
Model 5 *(5% $CaCO_3$)*	0.03795	0.97	0.0128

Figure 12 Model 1

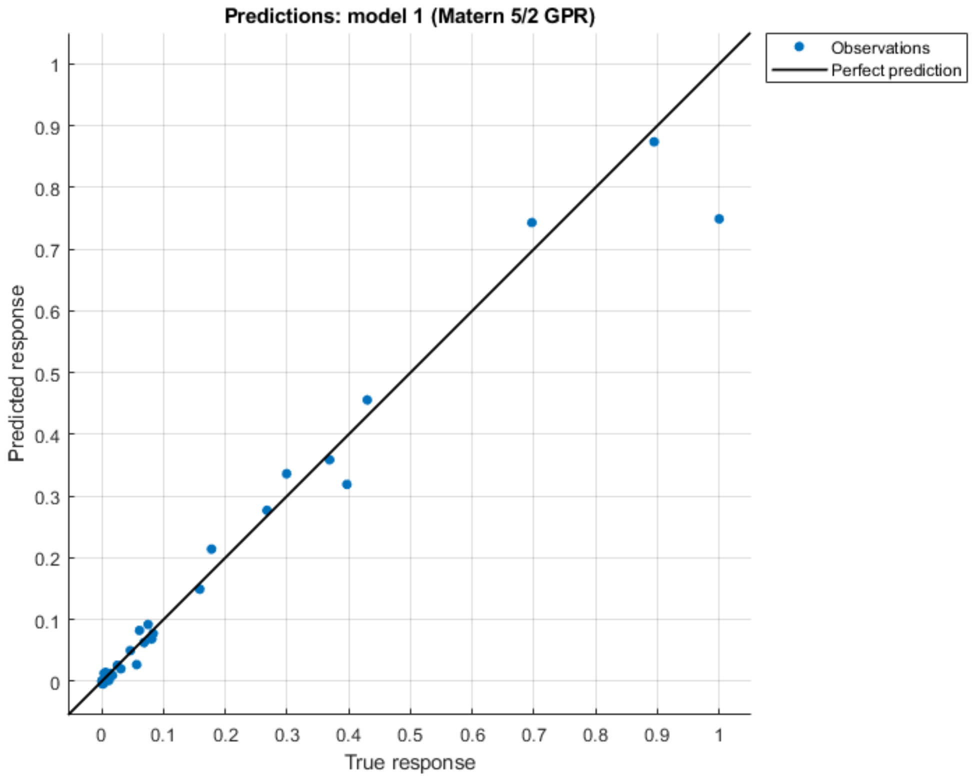


Figure 13 Model 2

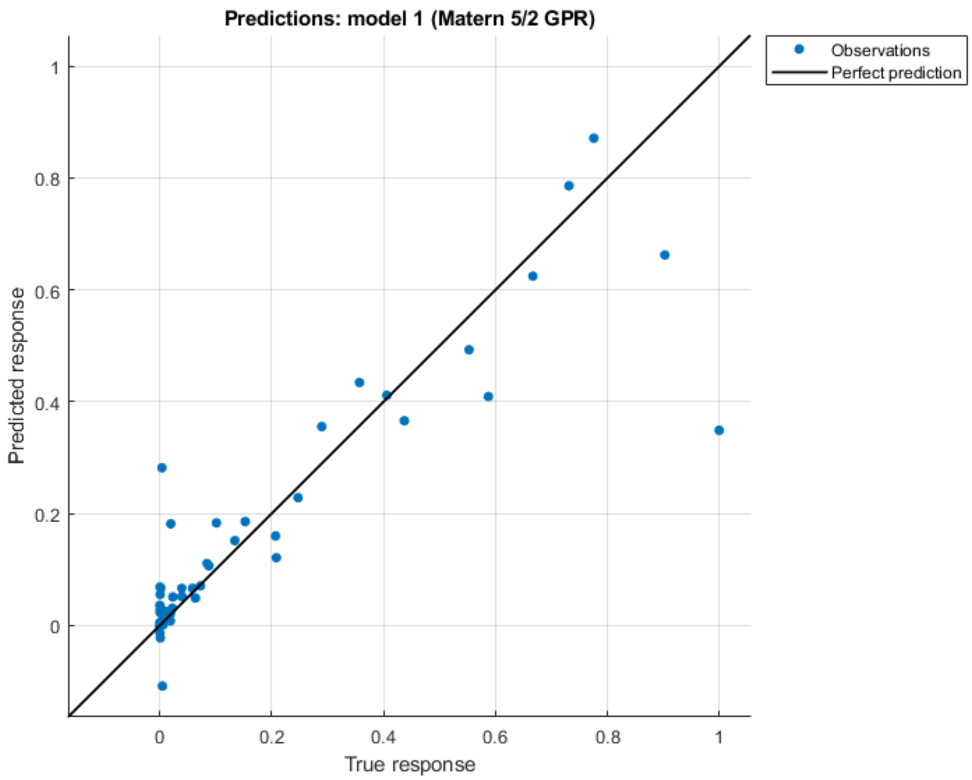


Figure 14 Model 3

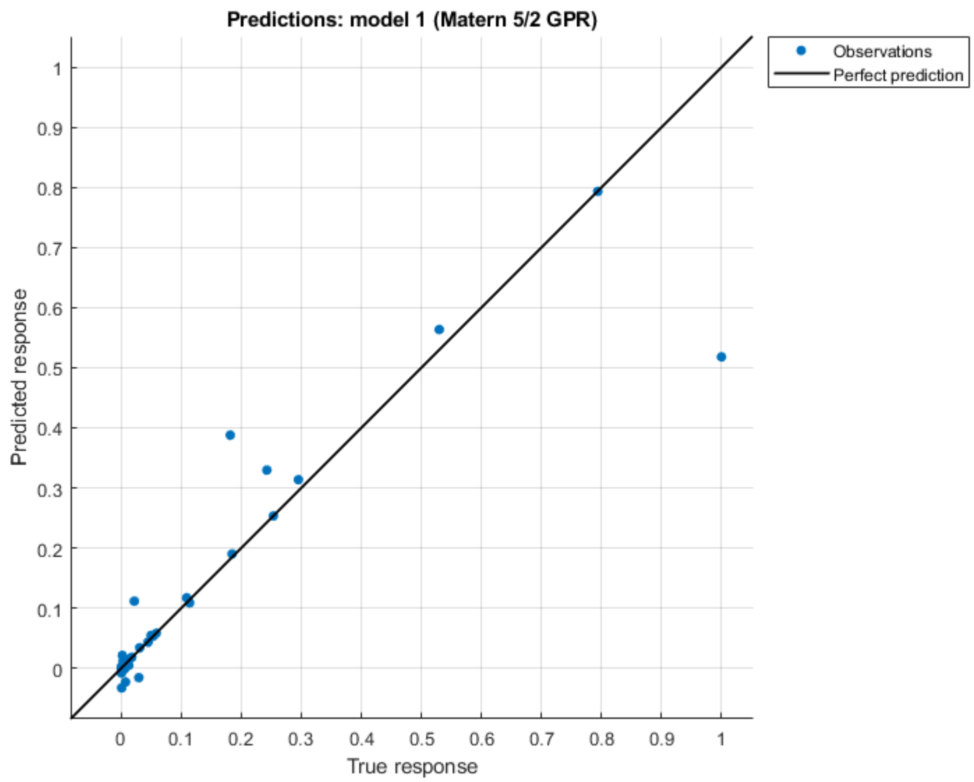


Figure 15 Model 4

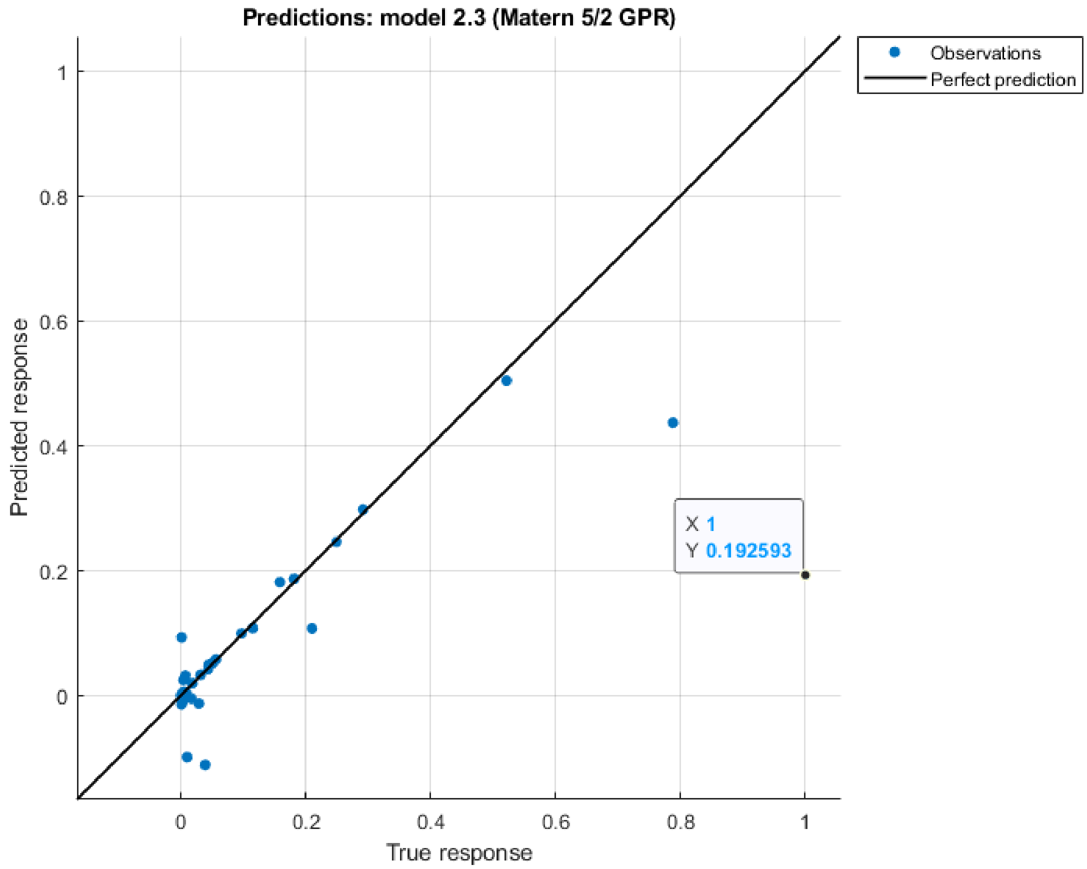


Figure 16 Model 5

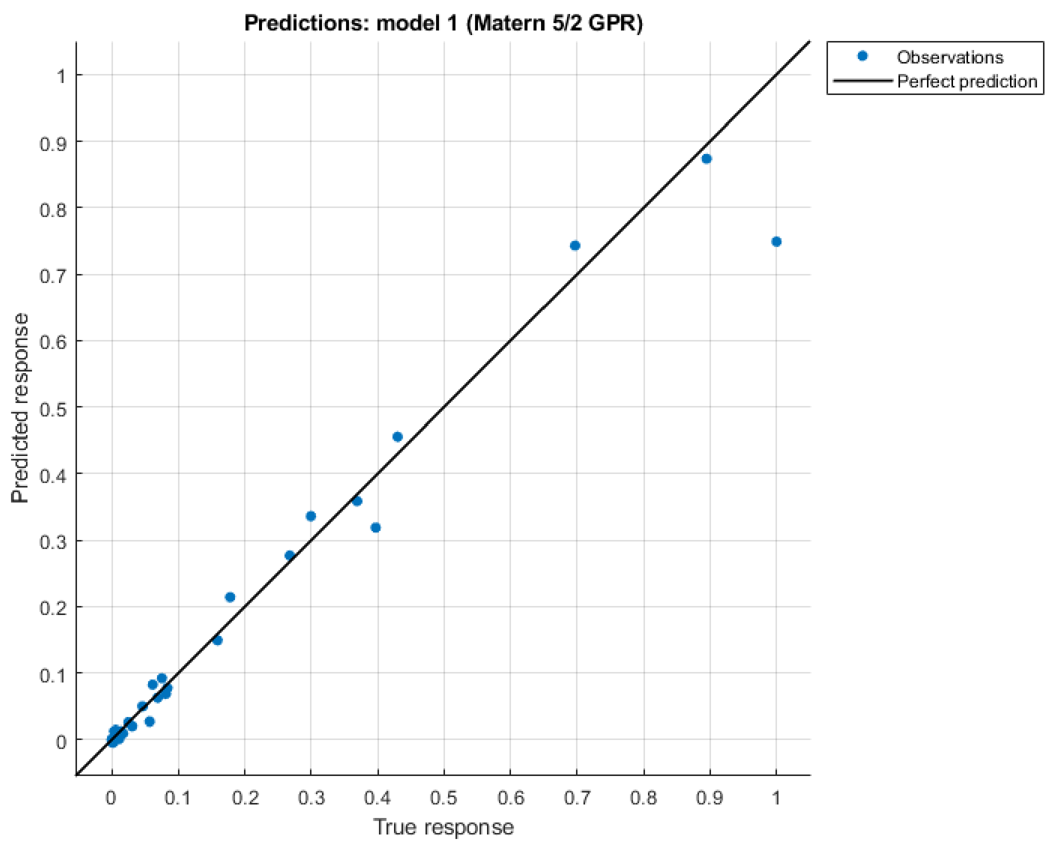


Table 3: Hyperparameters proposed model for modelling the vehicular traffic noise and their search space used for fine-tuning

Models	**Hyperparameters**
GPR	Sigma: 0.0001-45.2648 Basis function: Constant, Zero, Linear Kernel function: Non-isotropic Exponential, Non-isotropic Matern 3/2, Non-isotropic Matern 5/2, Non-isotropic Rational Quadratic, Non-isotropic Squared Exponential, Isotropic Exponential, Isotropic Matern 3/2, Isotropic Matern 5/2, Isotropic Rational Quadratic, Isotropic Squared Exponential Kernel scale: 0.3204-320.4

CHAPTER V

Conclusion and recommendation

This chapter summarizes the results obtained from this study and suggested recommendations.

Conclusion

This study has attempted to put forward a simple and yet straightforward comparison between four (4) commonly used modifiers, namely ENR, ASA, Al_2O_3, and $CaCO_3$, jointly classified as polymers and nanomaterials. With regards to the physical properties of the binder, it has been documented that generally, polymers and nanomaterials decrease the penetration of bitumen binders, which, on the other hand, has led to binders experiencing higher softening points and viscosity values. From the outcome of the storage stability tests, it was observed that all modified binders maintained a stable form after storage at high temperatures. In considering the rheological effects, properties such as rutting resistance at high temperatures, cracking resistance at low temperatures, and good performance grade have massively improved when these modifiers were introduced. From the rutting values obtained, it is evident that the binder incorporated with 5% Al_2O_3 nanoparticle had the greatest ability to resist permanent deformation and had the greatest toughness at high temperatures, although the 5% ASA polymer exhibited the greatest strength under thermal cracking from the isochronal plot. The binders, 5% ENR, 5% ASA, and 5% Al_2O_3 binders, had higher failure temperatures compared to the base asphalt and 5% $CaCO_3$.In conclusion, the use of polymers and nanomaterials has proven to be very important in the performance and durability of asphalt pavements by modifying the physical and rheological properties of the binders. The use of nanomaterials has proven to yield better properties when used as a modifier in asphalt binders, but its use is limited because of its uniquely complex production and subsequent usage in experimental research. This makes it quite expensive as many of them cannot be obtained or used when conventional methods and techniques are adopted. If conventional methods are found in the production process of nanomaterials, their widespread usage will revolutionalize the pavement industry.

Recommendation

It is recommended that more similar future research be conducted to verify the findings in this study. These studies should be extended to incorporate more and different polymers and nanoparticles that are used as modifiers in bitumen binders.

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NEAR EAST UNIVERSITY YAKIN DOĞU ÜNİVERSİTESİ

REF: 5/2022

ETHICS LETTER

TO GRADUATE SCHOOL OF APPLIED SCIENCES

REFERENCE: **EMMANUEL ACQUAH *(*20194240*)***

I would like to inform you that the above candidate is one of our postgraduate students in the Civil Engineering department he is taking a thesis under my supervision and the thesis entailed: **EVALUATION OF POLYMER AND NANOMATERIALS MODIFIED ASPHALT BINDERS AND MIXTURES: A COMPARISON APPROACH**. The data used in his study was our data obtained from experimental work previously.

Please do not hesitate to contact me if you have any further queries or questions.

Thank you very much indeed.

Best Regards,

Assoc. Prof. Dr. Shaban Ismael Albrka Ali

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