CHARACTERIZATION OF ASPHALTBINDER MODIFIED WITH NANOCOMPOSITE

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF APPLIED SCIENCES OF NEAR EAST UNIVERSITY

By
PESHAWA AMEEN SEDIQ

In Partial Fulfilment of the Requirements for The Degree of Master of Science in Civil Engineering

NICOSIA, 2018

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Peshawa Ameen SEDIQ: CHARACTERIZATION OF ASPHALTBINDER MODIFIED WITH NANOCOMPOSITE

Approval of Director of Graduate School of Applied Sciences

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

The study examined the performance and characteristics of unmodified and modified asphalt binders with Copper Oxide and Calcium Carbonate nanoparticles. The ASA-modified asphalt binder was evaluated in two different concentrations 3% and 5% of CuO and $CaCO_3$ by weight of bitumen. The physical properties were investigated through conventional tests including, penetration, softening point, and viscosity. The unmodified and modified binders were evaluated through dynamic shear rheometer for rheological properties of the asphalt binders. The properties of all samples were tested under different temperatures and with varying frequencies to observe the substantial changes for accurate results. The results of the study were outstanding and the modified asphalt binders observed to have increased resistance against deformation, improved durability, and least susceptibility to high temperature that can cause rutting of asphalt pavements. The penetration of ASA-modified asphalt binder with 3% Cu decreased while increasing the softening point to 56°C. The rotational viscosity of the 5% CuO and $CaCO_3$ binders significantly decreased with an increase in the temperature. The overall rheological properties also improved as the isochronal plots revealed that the stiffness of modified asphalt binders increased with increase in temperature at frequencies of 1 and 10 rad. The master curve of the ASA-modified asphalts with CuO and $CaCO_3$ outlined an increasing viscoelastic behavior. The rutting parameters outlined a significant resistance to rutting of modified asphalt binders at high temperature as compared to the control asphalt binder.

Keywords: ASA-modified asphalt binders; copper oxide and calcium carbonate nanocomposites; penetration; softening point; viscosity; dynamic shear rheometer

ÖZET

Bu çalışmada, Bakır Oksit ve Kalsiyum Karbonat nanopartikülleri ile modifiye edilmiş asfalt bağlayıcıların performansı ve özellikleri incelenmiştir. ASA ile modifiye edilmiş asfalt bağlayıcı, iki farklı konsantrasyonda CuO ve $CaCO_3$'ün ağırlıkça% 3'ü ve% 5'i olarak değerlendirilmiştir. Modifiye edilmemiş ve modifiye edilmiş asfalt bağlayıcıların özellikleri, penetrasyon, yumuşama noktası ve viskozite dahil olmak üzere geleneksel testlerle değerlendirildi. Asfalt modifiye edilmemiş ve değiştirilmiş bağlayıcıların reolojik özellikleri dinamik kesme reometresi ile değerlendirildi. Modifiye edilmemiş ve modifiye edilmiş asfalt bağlayıcıların fiziksel ve reolojik özellikleri, doğru sonuçlar için önemli değişiklikleri gözlemlemek üzere farklı sıcaklıklarda ve değişen frekanslarda test edilmiştir. Çalışmanın sonuçları çok barizdi ve modifiye edilmiş asfalt bağlayıcılar, deformasyona karşı daha fazla direnç, daha fazla dayanıklılık ve asfalt kaplamaların çentiklenmesine neden olabilecek yüksek sıcaklığa karşı en az duyarlılığa sahip oldukları gözlemlendi. ASA ile modifiye edilmiş asfalt bağlayıcının% 3 Cu ile nüfuz etmesi, yumuşama noktasını 56 ° C'ye çıkarırken azalmıştır. % 5 CuO ve $CaCO_3$ bağlayıcıların rotasyonel viskozitesi, sıcaklıkta bir artışla önemli ölçüde azaldı. Genel reolojik özellikler ayrıca, eşzamanlı parseller, modifiye edilmiş asfalt bağlayıcıların sertliğinin, 1 ve 10 rad frekanslarında sıcaklık artışı ile arttığını ortaya çıkardıkça, geliştirilmişlerdir. CuO ve $CaCO_3$ ile tüm ASA modifiye asfalt bağlayıcıların ana eğrileri, artan bir viskoelastik davranışı özetlemiştir. Rutting parametreleri, modifiye asfalt bağlayıcıların, kontrol asfaltı bağlayıcısına kıyasla yüksek sıcaklıkta çürütülmesine karşı önemli bir direnci açıkladı.

Anahtar kelimeler: ASA modifiye asfalt bağlayıcılar; bakır ve kalsiyum nanokompozitler; penetrasyon; yumuşama noktası; viskozite; dinamik kesme reometresi

TABLE OF CONTENTS

ACKNOWLEDGEMENTS ii
ABSTRACT iii
ÖZET iv
TABLE OF CONTENTS v
LIST OF TABLES ix
LIST OF FIGURES x
LIST OF ABBREVIATIONS xi

CHAPTER 1 : INTRODUCTION
1.1 Overview and Background 1
1.2 Problem Statement 4
1.3 The aim and objectives of the Study 4
1.4 Study Question 5
1.5 The Significance of the Study 5
1.6 Thesis Organization 6

CHAPTER 2 : LITERATURE REVIEW
2.1 Introduction 7
2.2 Efficiency of Asphalt for Construction 7
2.2.1 Low Cost 8
2.2.2 High Speed 8
2.2.3 Eco-friendly 8
2.2.4 Recyclable 8
2.2.5 Durable 8
2.3 Asphalt Binders Modified with Rubber 9
2.3.1 Dry method 9
2.3.2 Wet method 9
2.3.3 Terminal blend 9
2.4 Asphalt Binders Modified with Nanoparticles 10

2.5 Asphalt Binders Modified with SBS 14
2.6 Asphalt Binders Modified with Elvaloy 17
2.7 Modified Asphalt Binders 19
2.8 Cost-Efficiency of Asphalts for Preservation and Maintenance 22

CHAPTER 3 : METHODOLOGY

3.1 Experimental Design 25
3.1.1 Materials 25
3.1.2 Sample preparation.. 27
3.2 Experimental Procedures 29
3.2.1 Physical properties 29
3.2.2 Penetration test.. 29
3.2.3 Softening point 30
3.2.4 Rotational viscosity 32
3.3 Dynamic Shear Rheometer 34
3.3.1 Complex shear modulus 36
3.3.2 Phase angle 37
3.3.3 Isochronal plot 38
3.3.4 Rheological master curve 38
3.3.5Black diagram 38
3.3.6 Parameters of rutting 38

CHAPTER 4 : RESULTS AND DISCUSSION

4.1 Intoduction 40
4.2 Physical Properties 40
4.3 Rotational Viscosity 41
4.4 Rheological Properties 42
4.4.1 Isochronal plot 42
4.4.2 Rheological master curves 42
4.4.3 Black diagram………..……………………………………………………… 45
4.4.4 Fail Temperature 46

4.4.5 Rutting parameter 47

CHAPTER 5 : CONCLUSION AND RECOMMENDATION

5.1 Introduction 50

5.2 Conclusions 52

5.3 Recommendation for Future Research 54

REFERENCES 55

APPENDICES

APPENDIX 1 : Rheological Master Curves For Unmodified And Modified Asphalt 60

APPENDIX 2 : Curves Of Black Digram 64

APPENDIX 3 : Penetration Test 67

APPENDIX 4 : Viscosity Test 67

APPENDIX 5: Dynamic Shear Rheometer 69

LIST OF TABLES

Table 2.1: Particle Size Chart 10

Table 3.1: Physical and Chemical Properties of Asphalt Cement and ASA 25

Table 3.2: Physical and Chemical Properties of Copper Oxide Nanocomposites.......... 26

Table 3.3: Physical and Chemical Properties of Calcium Carbonate nanocomposites .. 27

Table 4.1: Physical Properties of ASA-Modified Asphalt Binder.................................. 40

LIST OF FIGURES

Figure 2.1: Moisture Susceptibility (a) SBR% (b) PS% 13

Figure 2.2: TEM of Asphalt modified with (a) 3% and (b) 5% of SBS 16

Figure 2.3: Penetration of Base and Modified Asphalt 20

Figure 2.4: Softening Point of Base and Modified Asphalt 21

Figure 2.5: Viscosity of Asphalt (unmodified & modified) at Different Temperatures 22

Figure 3.1: Flowchart of the study... 28

Figure 3.2 : (a) Penetrometer (b) Fluid Sample of Bitumen 30

Figure 3.3 : Ring and Ball Apparatus for Softening Point Test 31

Figure 3.4: Sinking Balls as Temperature Rises... 32

Figure 3.5: Brookfield Viscometer 33

Figure 3.6: Dynamic Shear Rheometer (DSR)... 35

Figure 3.7: DSR Sample Sizes 36

Figure 4.1: Rotational Viscosity at 135°C and 165°C 42

Figure 4.2: Isochronal Plot of the Complex Modulus G* at 1 Rad 43

Figure 4.3: Isochronal Plot of the Complex Modulus G* at 10 Rad 44

Figure 4.4: Complex Modulus Master Curve for Base and Modified Asphalt at the Reference Temperature of 52°C 45

Figure 4.5: Black Diagram for Unmodified and Modified Asphalt Binders 46

Figure 4.6: Fail temperatures of Modified and Unmodified Asphalt Binders 47

Figure 4.7: Effect of Temperature on Rutting Parameter of BASE and Modified Asphalt Binders.. 48

LIST OF ABBREVIATIONS

SBR	Styrene-Butadiene Rubber
SBS	Styrene–butadiene–styrene
GTR	Ground Tire Rubber
ENR	Exposed Natural Rubber
ASA	Acrylate Styrene Acrylonitrile
RAP	Recyclable Asphalt Pavements
APP	Atactic Polypropylene
OVMT	Vermiculite
OMMT	Montmorillonite
TEM	Transmission Electron Microscopy
MSRC	Multiple Stress Repeating Creep

CHAPTER 1

INTRODUCTION

1.1 Background

The asphalt binders are perceived as a value-added product that has a high level of production flexibility in the pavement. Asphalt binders with an improved characteristic like low volatility are obtained through refining and formulation phases. However, asphalt binders tend to have distinctive physical characterization with the development of new and more essential methods of testing and refining. The rheological tests were popularized in the 1990s for the construction of roads (Hunter, et al., 2014). Asphalt binders are used in 70% of the road construction and are made up of rock, sand, and aggregates combined with asphalt cement that is the binder (Yang & Tighe, 2013). Because of the technological and instrumental advancements, the asphalt binders are also studied for more specific compliance. The improving physical and rheological characterization of the asphalt binders also has great implications for the better performance of asphalt mixtures and asphalt binders for the pavements. The pavement performance has increased in terms of durability and long life because of the improved asphalt binders through the consistent and improving testing methods (Ali, et al., 2015). The asphalt binders modified with nanocomposites using the experimental design can be tested for pavement performance with different concentrations and in changing temperatures as studied by Ali, et al. (2016) that revealed that asphalt binders modified with nanocomposites were remarkable for performance and sustainability as observed and analyzed statistically using ANOVA. The study also determined the softening points, penetration and rheological limitations. The study also focused on storage stability and achieved positive results with high performance and resistance.

Asphalt binders can be studied for different behaviours when tested with different methods and distinctive compositions at different temperatures. The durability of the asphalt binders is easier to test because of the technological and advancement in the modeling techniques. The asphalt binders are better than the concrete and comparatively are less expensive, more reliable and durable with the construction of roads. The pavements can be made in a comparatively less amount of time, maintenance is low cost if needed and the durability is for the longer term. The concrete pavements were less durable, more time taking to construct and needed frequent maintenance (Hiroyuki, 2009).

The asphalt binders are commonly incorporated in designing the roads and pavements particularly in the developed countries like the United States, Australia, Canada and the European countries. The commonly used polymers with the asphalt binders include SBR, rubber, Elvaloy, and SBS. The modification of the asphalt binders with the nanocomposites to detain the rheological properties of the modified binders are done to predict the practical road performance. Yildirim (2007) revealed that the elastic recovery test is reasonable and practicable for predicting the future pavement performance through modified pavements. The rheological properties are important for predicting the performance of the modified asphalt indeed in the field but the characterization failure properties also play a significant role in determining the performance of the pavements through the modified asphalt binders (Anderson, Youtcheff, & Zupanick, 2000). Asphalt binders with nanocomposite are experienced with guaranteed durability and high performance in designing the pavements. It is observed that the performance of the asphalt pavements with the nanocomposite is better than that of the concrete or simple asphalt binders. The asphalt binders modified with nanocomposite are cost-effective and have high performance. The asphalt binders modified with the nanocomposite does not require a high cost for maintenance, and this is the reason that the market demand is pulling the modified asphalt binders almost in all developed and now in developing countries (Ali, et al., 2016).

Despite different materials incorporated in the construction of roads, asphalt binders are the most cost-effective and durable that they are used in most developed countries. The construction of pavements is a long process and often takes a long time and so is the maintenance. This is the reason that the developed countries have high quality and sustenance for the pavements is the use of the asphalt binders for the construction rather than the concrete. The asphalt binders modified with nanocomposite are proven to avoid rutting, creeping and fatigue cracking. The poor performance of the pavements with environment or traffic has and can be minimized with the help of modified asphalt binders. The issues of rutting and fatigue cracking are the result of extreme temperatures and/or heavy traffic load (Hiroyuki, 2009).

With the modified asphalt binders, the construction of the pavements has become more flexible and less time taking at a significantly reduced cost. The asphalt binders modified is a remarkable change in the construction techniques and the development process itself. Asphalt binders modified with the nano-materials are resistant to the extreme temperatures, rain, traffic load and other vulnerabilities that impact the performance of the pavements in long-term service life. The modified asphalt binders are not only enhanced for performance and quality but also to build more compatible pavements that are strong enough to overcome these vulnerabilities like fatigue cracking, rutting, and creeping. The asphalt binders modified with nanocomposites are tested for durability, and the tests revealed that the capacity of the construction material like that of the modified asphalt binders is perfect for designing the pavements and sustaining the transportation system (Yazdani & Pourjafar, 2012). The asphalt binders have been experimented for mechanical and physical properties that enhance the performance and stability of the pavements that are low-cost as well as high quality. A study conducted to investigate the impact of polymer-nanocomposite modified with asphalt binders outlined, the rutting can be minimized using distinctive penetration levels (Bayekolaei, Naderi, & Najad, 2017).

1.2 Problem Statement

The performance of asphalt pavement is affected by moisture, temperature, and traffic loads. The asphalt is modified with different nano materials to improve the performance but there is a need for more sustainable modified asphalt binders that can improve the properties of asphalt to resist damage by designing the asphalt binders modified with the suitable and appropriate nanocomposite. To test the efficiency of modified asphalt requires feasible time and cost. However, the human error can also be possible when conducting these tests. The measurements have to be precise and accurate. The readings recorded for each test and with each temperature must be appropriate to achieve the desired results.

This is also important because the asphalt binders are tested for durability with nanocomposite at different temperatures and with distinctive nanocomposites. Thus, obtaining only the accurate measurements helped to differentiate the most suitable composition for performance and sustainability.

1.3 The Aim and Objectives of the Study

The aim of the study is to enhance the quality of asphalt binders modified with Copper Oxide and Calcium Carbonate nanocomposite to achieve better performance despite temperature and exposures. To achieve this aim the following objectives will be following:

1. To investigate the effects on nanoparticles on the physical properties of asphalt binders.
2. To evaluate the rheological properties of modified asphalt binders
   To establish a comparative regarding the performance of nanocomposites on modified asphalt binders.

1.4 Study Questions

The study addressed the below-mentioned questions:

1. What are the benefits of adding nano-Copper Oxide and nano Calcium Carbonate to asphalt binder?
2. What is the best percentage of nano-Copper Oxide & nano Calcium Carbonate needed to modify the asphalt binder to get a better property than base asphalt binder?
3. Which of nanoparticles gives better results regarding asphalt binder modification?

1.5 The Significance of the Study

This study focused on nano Copper Oxide and nano Calcium Carbonate as nanocomposite modifiers to the base asphalt binders at two different concentrations of 3 and 5% for each concentration to check for temperature susceptibility to improve the resistance of asphalt binders against rutting. The study outlined all significant difference levels by describing all the extraordinary influences on dependent variables. This enhances the significance of the study for not just the theoretical but also the practical knowledge and implementation of the study aim. The DSR machine outlined the complex shear modulus G* with its significance as increased or decreased with different concentrations and with changing temperatures. The study holds a great significance for theory and practice as it experiments with a good range of tests, concentrations (weights), and temperatures.

1.6 Thesis Organization

The thesis followed the below design:

Chapter 1:

It is the introduction to the topic of the study. Chapter 1 presented the background, study problem, aim and objectives of the study. Lastly, it outlines the significance of the research with a thesis overview.

Chapter 2:

This is the review of the existing literature on the asphalt binders and their modification with nanocomposite. This chapter helped in finding the study gap that enhances the significance of this study and makes it more relevant for the future study in this area.

Chapter 3:

It outlines the theoretical framework and demonstrates the in-depth knowledge of the asphalt binders, nanocomposite, and their characteristics.

Chapter 4:

It presented the findings and discussions of the study. Chapter 4 outlined the results and analysis of the study including the results obtained from tests in an organized manner.

Chapter 5:

It is the last chapter of the study and concluded the investigation with implications and recommendations for future work. The conclusions and recommendations were presented based on the study findings and inferences based on how the things can be improved for the future study that could not be achieved through this study. .

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The appreciative viscoelastic properties of the asphalt allow the construction companies to construct the pavements and runways with asphalts. The increasing use of asphalt binders in the construction sector is attracting not just the interest of business developers and investors but also there is an increasing popularity of asphalts in research and development. The asphalts have varying chemical, physical and rheological properties that could be enhanced further with modification generally and commonly with rubber, SBR, Elvaloy, and SBS. The asphalt binders are the organic composites. However, these properties can transform with time and external effects of extreme environmental changes like temperatures, traffic and other. The studies have been done, and there is a still Research & Development process going on to observe and sustain the most effective composition for high durability and sustainable performance. Asphalt binders are now more improved, efficient and safer in term of environmental sustainability. In comparison, the negative effects of changing temperature, oxygen and the harmful ultraviolet rays of the sun. These results in aging that affects the long-term performance and durability of the pavements. Therefore, it is important that the asphalt binders can be modified with different nanocomposites to increase their effectiveness and efficiency.

2.2 Efficiency of Asphalt for Construction

The efficiency of asphalt for the construction of roadways, pavements, highways validated long ago. The developing countries are using asphalts in the construction and maintenance of the pavements. The construction of the pavements is not only comparatively low cost but also the time of construction is reduced, the construction is eco-friendly and safer for the labors. The asphalt pavements are more durable and have high performance as compared to concrete. The most significant and substantial element of asphalt is that it is recyclable that makes it a green technology that is safer for the environment. Asphalt is the only choice for e construction and development of sustainable and reliable pavements.

2.2.1 Low cost

Asphalts are a low cost yet highly compatible materials used in the construction of roadways, runways, and pavements. They are widely acknowledged as the most sustainable and durable construction materials that are obtained from petroleum refining.

2.2.2 High speed

The construction of the pavements is increased drastically through asphalt. The construction of roads with concrete took years to develop sometimes because of the cost and sometimes because of the lack of transportation ways that compelled the construction authorities to delay the process because it was time taking.

2.2.3 Eco-friendly

The asphalts are greener and environment-friendly materials. Approximately 90% of the 5.2 million km of roads in Europe are asphalt paved. Around 44% of goods are transported through these pavements still these roads are sustainable and are accelerating the economic benefits (Kowalski, et al., 2016).

The construction of new roads has many implications, consumption of considerably large material, energy, environmental threat and of course the increasing prices of oil and petroleum. In such a situation, the construction of pavements with asphalt assists in many ways. It is essential that the asphalts modified with different additives must be used for high performance and optimal delivery of service. It is important that the asphalt for construction of roads be used with construction and demolition waste (C&DW), and bio-binder obtained from vegetable oil. The more ecologically oriented asphalts are more reliable and effective (Fini, Al-Qadi, You, Zada, & Mills-Beale, 2012).

2.2.4 Recyclable

Asphalts are safer than any other materials used in construction. Recyclable asphalt pavements (RAP) are safer and are friendly to the environment. Asphalts are a green material that does not harm the environment during or after construction (Kowalski, et al., 2016).

2.2.5 Durable

Asphalt pavements are more durable and reliable as compared to concrete roads. The asphalt pavements are effective and have a long service life. They can be modified with additives to improve the physical and rheological properties that can enhance their durability and increase the benefits associated with asphalt pavements (Presti, 2013).

2.3 Asphalt Binders Modified With Rubber

Asphalt binders are modified commonly with rubber. The modification asphalt binders with rubber started in the 1800s, and many countries tried to modify the rubber of the tires. However, these modifications were not much successful. The modification of asphalts with rubber included several methods as:

2.3.1 Dry method

It is easy to handle and requires fewer materials. It does not need much equipment for its processing, and the ground rubber can be directly used in the asphalt plant. It is advantageous and simple as compared to other methods (Hernández-Olivares, Witoszek-Schultz, Alonso-Fernández, & Benito-Moro, 2009).

2.3.2 Wet method

The wet method for the modification of asphalt, crumbed rubber is used. The crumbed rubber is mixed at a high temperature with the asphalt binder (Presti, 2013).

2.3.3 Terminal blend

The terminal blend is a conventional method that is used for modification of asphalt binder with rubber. It improves viscosity and elasticity of the modified asphalt that enhances permanent deformation. The rubber is blended with a binder for optimal results (Katman, Ibrahim, Karim, Koting, & Mashaan, 2016).

Updyke and Diaz (2008) observed the rubberized asphalt concrete and its use. The asphalt modified with ground tire rubber GTR for the construction of pavements. The study noted that the rubberized asphalt pavements in the south were remarkable environment-friendly. At the same time, the modification of asphalt with rubber provided an opportunity for the tire manufacturing companies to reuse the old tires for better and improved roadways. This is not only useful to the construction sector but also opened opportunities for the tire manufacturing industries. Also, the people could also benefit from the improved and green roads.

However, accepting and propagating the use of GTR was among the biggest challenges of the industry. This was because of the previous rubber modification failure, and the transportation department was hesitating to allow the construction of pavements with rubberized asphalt. The later years of resaerch and development, the Transportation Department of Missouri funded the testing of rubber modified asphalt, and the results were outperforming even beyond the expectations. The particle was named as the tire rubber modified asphalt cement TRMAC that was measured between 0.5 to 1.0 microns. The particle size and the microns are compared in Table 2.1.

Table 2.1: Particle size chart (Updyke & Diaz, 2008)

Particle Size	(microns)
1/16 inch	1,680
(0.0661”)	
40 mesh silica sand	425
(0.0165”)	
200 mesh sieve	75
(0.0029”)	
Mold	3-12
Talcum Dust (baby powder)	0.5-50
(0.0020”)	
Anthrax	1-5
TRMAC™ 25%	0.5-1

Tire Rubber Asphalt Cement (0.0000394”)	
Sea salt	0.035 - 0.5

Using asphalt modified with recycled rubber can be effective for engineering, economic and environmental security. The construction of pavements is a complex process and so is costly. The use asphalt in the construction roads has made the life better and this is reviewed in-depth by Presti (2013) that revealed, recycled tire rubber RTR is one of the increasingly used product in the civil engineering field. The RTR modified asphalts are more environmentally friendly and can help in reducing the cost by increasing the benefits of the construction and manufacturing companies. The study also revealed that the rubber modified asphalts have better road performance and durability. The technology and specific techniques have also evolved with a time that can help in the production and storage of RTR modified asphalts.

Similarly, a study conducted by Al-Mansob et al. (2017) revealed that polymers modified asphalts have better rheological and physical properties. The enhanced physical and rheological properties of asphalts add to the performance and durability of the pavements constructed from asphalt. The study observed that nanoparticles such as nano alumina could enhance the compatibility of the asphalt modified with exposed natural rubber (ENR). However, their modification can yield effective results with appropriate and adequate methods. The study investigated the effects of ENR, and nano alumina was compatible to improve the rheological properties of asphalt binder as the combination of ENR with nano alumina resulted in a better dispersion. The study observed the changes in rheological properties through dynamic shear rheometry tests. The results of the study revealed that the temperature susceptibility was reduced by nano alumina. The modification also facilitated the increase in viscoelasticity, adhesion, and stiffness behavior of the asphalt binders. In addition, the results also demonstrated improved rutting resilience among the binders at a high temperature. Lastly, the most suitable percentage of nano alumina was observed as 6% at which polymer modified asphalt outperformed in comparison to the asphalt without nano alumina.

2.4 Asphalt Binders Modified with Nanoparticles

Styrene-Butadiene Rubber (SBR) belongs to the family of Rubbers that are commonly used to modify asphalts and to enhance the resistance against the temperature susceptibility, it's important that the asphalts are modified with nanoparticles that can resist rutting at high temperature and crack at low temperature. Since the 1960s, the EU states have built roadways and highways using asphalt that are modified with polymers. The asphalts modified with polymers are essential for building temperature resistance and also resilience against other vulnerabilities like the traffic loads, environmental changes and other distress.

Similarly, in 1993, France built roads that used 8% of polymer modified asphalt. Because of proven durability and sustainability in the pavement construction; Brazil in the 1990s also started to use asphalt modified with the polymer in the construction of roads and pavements. However, polymer modified asphalt is popularly used nowadays in almost all countries around the globe. The increasing use of polymer modified bitumen is due to it enhances properties that resist aging, rutting, fatigue cracking and abrasion at extreme temperatures.

A study conducted by Abdul-Mawjoud and Thanoon (2015) the performance of asphalt binder modified with SBR and polystyrene (PS) modified asphalt binders. The study observed the performance of the asphalt by modifying with four different concentrations, 1, 3, 5, and 7%. The study compared the properties of both control and modified asphalts. Different tests were conducted to test the properties of the asphalt, namely penetration, softening point, temperature susceptibility, ductility, and percent loss of heat and air. The Marshall quotient and Marshall stability tests with tensile strength, compressive strength, and flexible strength were conducted. The results of the study observed that the asphalt modified with SBR and PS outperformed than that of the conventional asphalt. Moisture and temperature susceptibility was reduced and 5% concentration was observed as that of SBR and PS to be ideal for optimal performance when modified with asphalt.

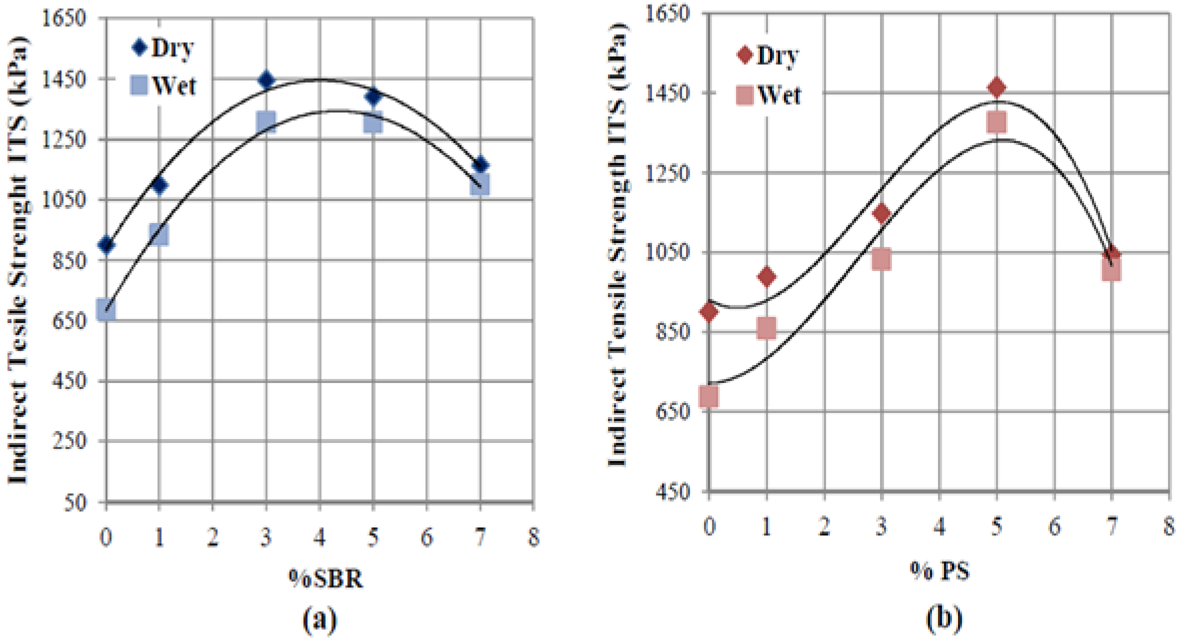


Figure 2.1: Moisture susceptibility (a) SBR% (b) PS% (Abdul-Mawjoud & Thanoon, 2015)

Figure 2.1(a) and (b) shows the tensile strength of SBRMABs and PS-MABs. The results demonstrate that the conventional asphalt had a moisture susceptibility of 76%. The tensile strength for SBRMAB was noticed to be 94% and for PSMAB was observed as 97% at 7% concentration. This means that the addition of SBR and PS to asphalt binder enhanced its capacity against moisture susceptibility as compared to that without SBR and PS (Abdul-Mawjoud & Thanoon, 2015). Though, there are many different modifiers that enhance the properties of asphalt to build resilience; polymers are among the most capable additives that can bring about substantial results. The polymers can distribute/scatter well in the asphalt and helps in improving the chemical composition of the asphalt. Polymers have four main types including, plastics, fibres, elastomers, and additives.

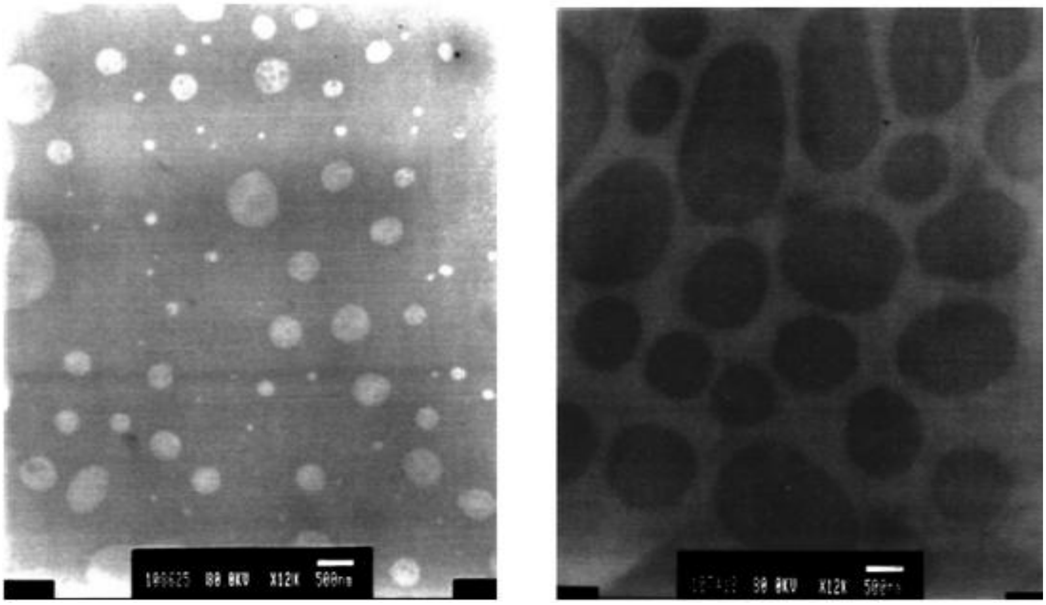
Similarly, a study conducted by Hussain, Ghaly, and Ibrahim (2008) observed the performance of hot mix asphalt for the maintenance of the pavements. The study outlined that overlay is one of the quickest and reliable techniques for the maintenance of distresses pavements. The study focused on thin hot mix asphalt as essential for the overlay. The study modified asphalt with atactic polypropylene (APP) at five different concentration of 3%-7% and also with one rubber percent of SBR and tire rubber. The study observed the penetration, softening point penetration temperature susceptibility and penetration index with dynamic viscosity and tensile strength. The performance of the modified and conventional asphalt was determined using Marshall and wheel tracking test.

The results of the study outlined that the properties of both the asphalts improved through the modifiers. 6% was observed to be ideal for APP modified asphalt. Moreover, the tensile strength of the APP was improved by adding 1% rubber at the low temperature. Marshall stability improved by 35% and the overall resistance to rutting enhanced by 84.3% with 6% modifier concentration. In addition, a study conducted by Tabatabaei, Kiasat, and Alkouhi (2013) observed the impact of SBR on the properties of SBR modified asphalt binders. The study outlined that using bitumen with hot mix asphalt, it is important to have some specific features and to achieve these characteristics, bitumen can be modified with polymers to improve the rheological properties essential for using it with hot mix asphalt. The study modified the properties of bitumen using SBR with three different concentrations of 3%, 4%, and 5%. The results of the study revealed that bitumen with 5% modification of SBr has outperformed as compared to others (Tabatabaei, Kiasat, & Alkouhi, 2013).

2.5 Asphalt Binders Modified with SBS

The impact of extreme temperatures results in rutting which is studied and analyzed through research and development. The asphalt binders modified with polymers and additives have been investigated to increase the tensile strength of the asphalt binders against the rutting from extreme temperatures. These studies have been quite useful and outlined substantially remarkable results. However, traffic and heavy traffic loads are other hazards to the performance and durability of the pavements. The heavy traffic loads result in the fatigue cracking and abrasion. The rapid distresses and deterioration of the pavements not only increases the cost of maintenance, but it is also affecting the further advancement of asphalts in research and development. The increasing pressures of tires require satisfactory engineering properties of the asphalt to resist and overcome the challenges posed by temperatures and traffic (Singh, Kumar, & Maurya, 2013).

Therefore, asphalts modified with polymers are studied significantly in-depth to improve the mechanical properties of the asphalt. Styrene–butadiene–styrene (SBS) is one of these polymers that can be used effectively as a modifier to improve the resistance of the asphalt against fatigue cracking and rutting. It has excellent engineering properties and low cost which enables the construction companies to use SBS in the construction and development of pavements and roadways (Zhuang, Li, Zhao, & Cai, 2017). SBS is a compatible and reliable polymer that is used in the development of highways and pavements for a long time. It has ensured high performance at not only high but low temperature as well. However, its properties are different from that of asphalt. To improve the compatibility of SBS with that of asphalt, different components can be used effectively as studied by Wang, Yi, and Yuzhen (2010) that observed that isolation experiment with intrinsic viscosity is essential to obtain the compatibility between SBS and asphalt through colloidal instability index (CI) (saturates+aromatics)/ (aromatics+resins). The results of the study revealed that sufficient scattering of the components like resins, aromatics and saturates is one of the fundamental factors to attain high compatibility and performance (Wang, Yi, & Yuzhen, 2010). Furthermore, it is also observed that the petroleum asphalt works as a perfect binder in constructing roads and pavements to ensure adhesive protection to the aggregates. The rheological behavior of the asphalt binder is not simple. It can have increased viscosity and/or elastic according to the change in load and temperature. It could and must be viscous when mixed with aggregates at high temperature and should be stiff at service to prevent rutting. Similarly, this stiffness is not effective at low temperature to prevent fatigue cracking. Therefore, the rheological properties play a major role in determining the performance of the asphalt binders in the field (Singh, Kumar, & Maurya, 2013). A study conducted by Chen, Liao, and Shiah (2002) analyzed the engineering and morphology properties of the asphalt binder modified with SBS triblock copolymer through transmission electron microscopy (TEM), dynamic shear rheometer and viscometer.



(a) (b)

Figure 2.2: TEM of Asphalt modified with (a) 3% and (b) 5% of SBS (Chen, Liao, & Shiah, 2002).

The study observed that by increasing the percentage of SBS, copolymer gradually became dominant. This transition leads to the transformation in SBS-modified asphalt’s engineering properties. The critical network between polymer and asphalt formed with an optimal SBS content. The formation of critical network resulted in increasingly complex modulus that is essential for resisting rutting at high temperature. The study proposed a Kerner model equation for predicting the modified asphalt's complex modulus at high SBS concentration as the Kerner model was inadequate at low SBS concentrations for estimating the rheological properties as shown in Figure 2.2 (Chen, Liao, & Shiah, 2002).

Although the natural/conventional asphalts are outperforming for many years, the growing loading rate and extreme temperature have proposed the need to be modified with additives to overcome distress and deterioration. Conversely, it is also important to maintain compatibility between asphalt and the polymers. A study conducted by Pamplona, et al. (2012) observed the impact of SBS and SBS-nano-clay on the rheological properties of the asphalt binders. The rheological properties of the asphalts are important in determining the capability of the asphalt to resist rutting and fatigue cracking which is a common challenge in the service and durability of the asphalt pavements in the field. The results of the study revealed an increase in the dynamic modulus of the modified asphalts with a reduction in the phase angle. This is substantial for avoiding and resisting permanent deformation. The study achieves appropriate viscosity, temperature susceptibility, and penetration with the nano-clays, vermiculite (OVMT) and montmorillonite (OMMT) with SBS-modified asphalt. The study also revealed the reduction in cost as the polymers can be replaced with low-cost nano-clays to achieve remarkable rheological properties. Furthermore, storage stability was also commendable with OVMT. However, the major obstacle in using SBS for pavements was the phase separation (Zhuang, Li, Zhao, & Cai, 2017).

2.6 Asphalt Binders Modified with Elvaloy

The asphalt binders are the most reliable and durable source of pavement construction and their efficiency is even enhanced when they are modified. The modified asphalts are capable of improving the field performance and in-service life of the pavements. The improvement in the rheological properties of the asphalt binders can also be improved through modification with crude oil and/or redesigning the refining process. Asphalts are a petroleum refinery product, and so it can be improved for performance with the refining process. The modified asphalt binders have proven performance and service sustainability. There are many modifiers that improve the properties and ultimately increase their performance of the asphalts against thermal cracking, fatigue cracking, rutting, and abrasion. Elvaloy is one of another commonly used modifier with asphalt binders that ensure high performance and sustainability. It is studied that to enhance the properties of Elvaloy-modified asphalt and glycidyl methacrylate molecule plays an important role in the formation of a stable polymer-asphalt system at high temperature. Elvaloy is also studied to improve the rheological properties of asphalt binders as observed by MSCR tests. The Elvaloy-modified asphalts also impact the sensitivity of asphalt to aging and reducing it for high performance (Delgadillo, Bahia, & Lakes, 2012).

A study conducted by Domingos and Faxina (2013) analyzed the rheological properties of asphalt binders modified with elvaloy and polyphosphoric acid (PPA) through a series of MSCR test. The study conducted the experiments with different temperatures, 52°C, 58°C, 64°C, 70°C and 76°C. The results of the study revealed that the modified asphalt binders had the highest percent recoveries (R) values and significantly low non-recoverable compliances (*J*nr) values. However, the results found the lowest sensitivity to a rapid increase in the level of stress in the asphalt mixture. The study found that the results were more favorable for asphalt modified with Elvaloy and PPA. Therefore, Elvaloy is a significant modifier that can increase the performance of the asphalt binder significantly, but asphalt with PPA with asphalt can also be considered as an alternative.

Similarly, a study conducted by Jasso, et al. (2015) observed the rheological and mechanical properties of natural asphalt when modified with elvaloy, SBS, and PPA. The study observed the impact of two different polymer groups on the properties of modified asphalt. The study observed the modification of elvaloy asphalt with and without PPA. The second group observed was with the SBS. The study tested rheological properties with steady-state shear viscosity and small-amplitude oscillations. Thus, the results of the study outlined a complex behavior at 60°C when the asphalt binder modified with elvaloy and PPA was blended with SBS through steady-state shear viscosity. In addition, the asphalt binder demonstrated a stiffening effect with the addition of elavloy and PPA. The addition of SBS leads to a network that improved the rheological properties of the modified binder. The study revealed that this effect was used for warm climates as it was substantially resilient to deformation. The modification led to higher elasticity at a higher temperature which mitigates the challenges of rutting and deformation (Jasso, et al., 2015). Furthermore, a study conducted by Topal (2010) evaluated the properties of asphalt modified with elvaloy 3427, elvaloy 4170, evatane 2805, and plastomeri polymers. The results of the study revealed that the modification of the bitumen with polymer improved the penetration, softening point, and temperature susceptibility. The study also found that there a strong relationship between the polymer's percent area distribution and its content. Therefore, elvaloy is a significant modifier that substantially improves the conventional properties of the asphalt binder for better performance and resistance. Elvaloy is noted for enhancing the properties of the asphalt binders that help in the high and low-temperature vulnerabilities.

2.7 Modified Asphalt Binders

Asphalt modified with ASA polymer and aluminum oxide additives have also been under consideration and can impact on the binder performance. This is also popular in research and development with a contingent consideration being given by the construction authorities to improve the in-service properties of the asphalt. The additives can play an essential role in improving the temperature susceptibility, compatibility and resilience among the modified asphalts. The polymeric additives can enhance the durability and performance of the asphalts to much extent. This is the reason that polymeric nanoparticles are popularly adopted in the construction of roads, pavements, highways, and runways frequently.

A study conducted by Mubaraki, Ali, Ismail, and Yusoff (2016) analyzed the rheological properties of asphalt binder by modifying with ASA and aluminum oxide nanoparticles with three different concentrations of 3%, 5%, and 7%. The study evaluated the properties and conducted viscosity, storage stability, frequency creep and multiple stress creep and recovery (MSRC) tests.

Furthermore, the results of the study revealed that the rheological properties of the asphalt modified with ASA and nanoparticles of aluminum oxide were substantially improved. The complex modulus also improved significantly with the increase in the concentration of modifiers. For 5% ASA and 5% aluminum oxide, the improvement was 63.70% and 71.12% respectively. These improvements were observed at 75°C. Similarly, the modified asphalt binders were observed for great rutting resistance at high temperature. The modified asphalt binders were also observed to have a creeping recovery of 69.23% and 62.53% approximately for ASA and aluminum oxide respectively. It can be concluded that the modified asphalt binders with ASA and aluminum oxide were resilient to high temperature with 5% concentration as most suitable for the modification. Asphalt binders are effective for resisting heavy traffic load. The safer roads ensure the safety of the drivers. Therefore, the asphalt binders are used in the construction of roads and highways to ensure safety and security. The roads that undergo rutting and fatigue cracking could be hazardous and thus impact the society. Asphalt binders have been used in the construction of roads to avoid the negative impact of temperature and a heavy load of traffic so that the roads and highways can be durable and sustainable.

A study conducted by Albrka, Ismail, Yusoff, AlHamali, and Musbah (2016) revealed that the natural asphalt lacks resistance against extreme temperatures and traffic loads. Therefore, it is important to modify the asphalt for improving the performance properties and build resilience. The study analyzed the properties of controlled and modified asphalt with ASA polymer through dynamic and creep tests. The increase in penetration and the decrease in softening point results in better temperature susceptibility among the modified asphalts. The study observed penetration as 69% with modification as shown in Figure 2.3.

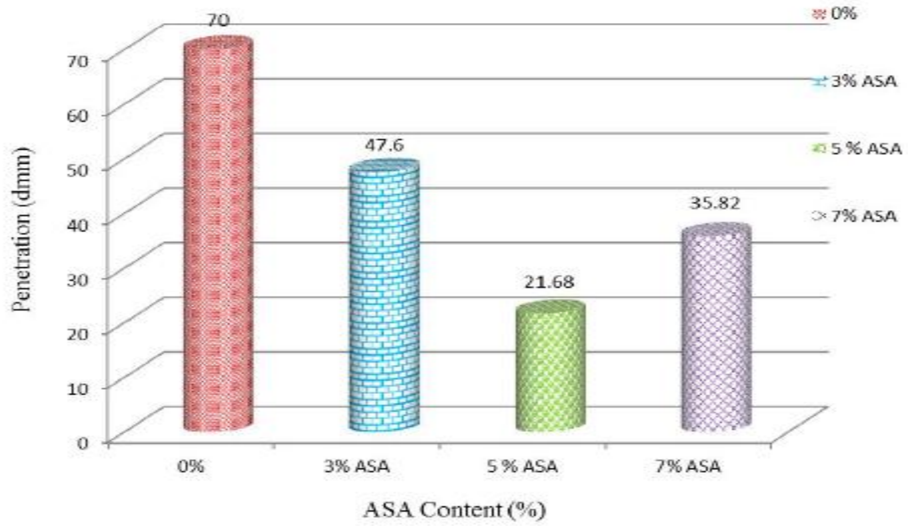


Figure 2.3: Penetration of base and modified asphalt (Albrka, Ismail, Yusoff, AlHamali, & Musbah, 2016)

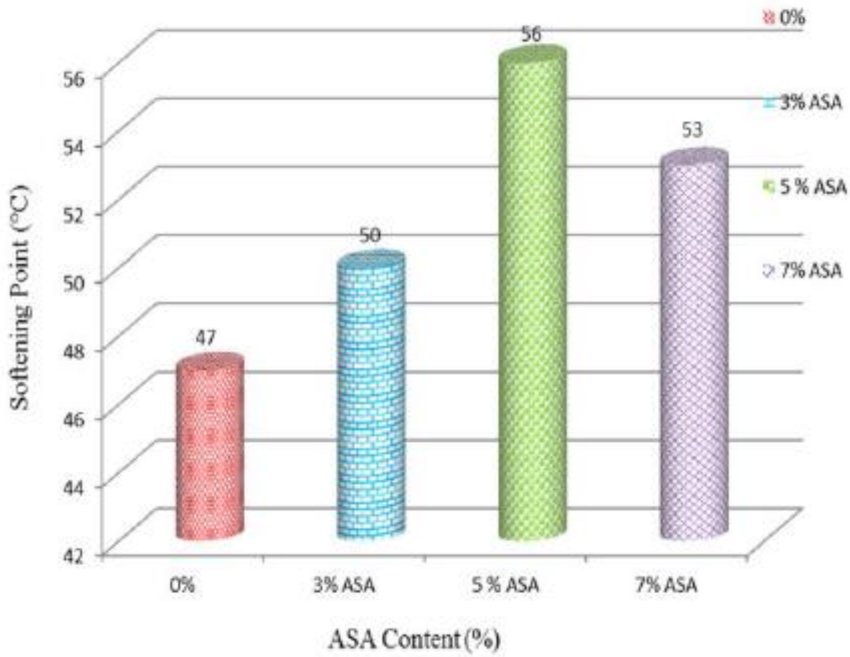


Figure 2.4: Softening point of base and modified asphalt (Albrka, Ismail, Yusoff, AlHamali, & Musbah, 2016)

Furthermore, the decrease softening point as 19% at 5% concentration. The results demonstrated in Figure 2.4 indicates that the stiffness of the asphalt is increased with the 5% ASA modification. This means that the stiffness is better than that of the base asphalt. Despite slightly changing with the addition of ASA as 7%, the results are still better than that of natural asphalt. The study concluded that the ASA polymer is effective and efficient to improve rutting resistance against high temperature at 5% concentration with asphalt binders (Albrka, Ismail, Yusoff, AlHamali, & Musbah, 2016).

Similarly, a study conducted by Ali, Ismail, AlMansob, and Alhmali (2017) evaluated the performance of asphalt binders modified with aluminum oxide and Calcium Carbonate nanoparticles. Therefore, the high-temperature properties of the controlled and modified asphalt binders can be tested using DSR and viscosity tests to ensure sustainability. The study modified asphalt binders with aluminum oxide and Calcium Carbonate nanoparticles with three concentrations as 3%, 5%, and 7% by weight of asphalt binder.

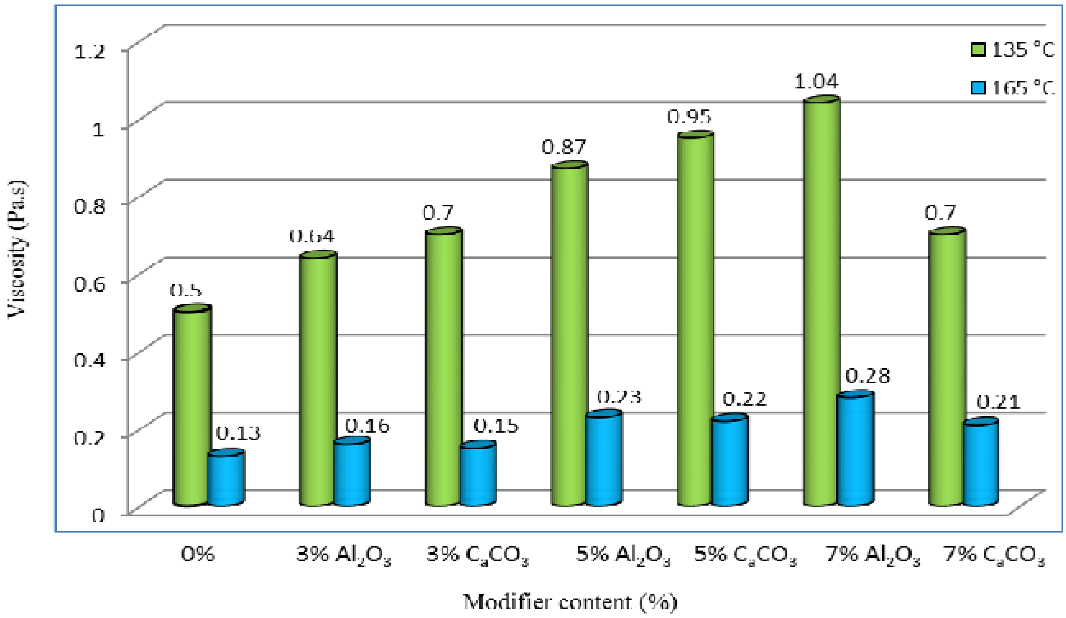


Figure 2.5: Viscosity of asphalt (unmodified & modified) at Different Temperatures (Ali, Ismail, AlMansob, & Alhmali, 2017)

The results of the study observed that there was a substantial change in the high-temperature properties of the asphalt binders modified with aluminum oxide and Calcium Carbonate. Moreover, the viscosity of the asphalt binder improved 108% and 90% by aluminum oxide and Calcium Carbonat respectively. Similarly, storage stability and compatibility also increased with an increase in the temperature of 135°C and 165°C. The results are shown in Figure 2.5. The stiffness increased while increasing the number of modifiers at 5%. The modified asphalt binder observed to have better rutting resilence. Aluminum oxide outlined enhancement of 388.89% and Calcium Carbonate as 73.07% approximately.

2.8 Cost-Efficiency of Asphalts for Preservation and Maintenance

The unpaved road is exposed to surface loss as a load of traffic increases. The roads need pavement when the traffic load increases from 150-400 vehicles per day (vpd). However, it is almost impossible and costly for the local agencies especially in developing or underdeveloped countries to pave the roads according to the traffic need. Therefore, it is important to consider the means and ways that could preserve the surface and surface distress which is cost-effective and reliable. A study conducted by Franke and Ksaibati

(2015) deliberated on recycled asphalt pavement (RAP) in several applications of highway construction and maintenance. The study analyzed various methods and compared the cost-efficiency for a more reliable way for maintenance on a budget. Dust loss, haul, layer coefficients and a decreased need for virgin aggregates were among the factors considered for analyzing the cost and benefits. Three case , the results of the study revealed that RAP is 100% reliable and can be used as a base. This can be stabilized with cement. The study observed some additional benefits of RAP. The study demonstrated that RAP has high resistance modulus and elasticity. For example, Lincoln Avenue in Urbana, USA was constructed from RAP. This indicates that RAP is a reliable base and has field performance with a cost-efficiency. The study found that remarkable dust reduction of $7.75/tonne of RAP. This means that RAP can save and cut on the maintenance cost as well. In addition, the application to observe savings from virgin aggregates was observed to be $11.07/tonne and the material cost was saved up to $45.07/tonne (Franke & Ksaibati, 2015). Similarly, a study conducted by Al-Mansob R. A., et al. (2017) revealed that road distress costs a lot for its maintenance. The study emphasized the fact that the maintenance cost could be decreased and/or controlled if the behavior and properties of the asphalts are understood properly. However, technology has played a substantial role in analyzing the properties and behaviors of asphalt with modifications of different nanoparticles. Therefore, the study discovered that polymers are the most suitable modifiers for asphalt to improve the properties and behavior of reducing the maintenance cost as the pavements are more resistance temperature and traffic. Furthermore, the permanent deformation improved at high temperature with the modification of epoxidized natural rubber (ENR). The study focused on the wet process for testing and found that asphalt modified with ENR was somewhat susceptible in the presence of water. The study emphasized on the fact that the performance of the roads and highways can be increased against major distresses and so is the maintenance cost with ENR modified asphalt (Al-Mansob R. A., et al., 2017).

A study conducted by Yao, et al. (2012) revealed that complex shear modulus and viscosity of the asphalt mixtures increased remarkably with non-modified nano-clay and when added to polymer modified nano-clay observed to decrease to some extent.

However, the polymer modified nano-clay also observed to have better resistance to rutting and cracking as compared to non-modified nano-clay. The asphalt binder was controlled PG-58-34 and the concentrations were 2% and 4%. The study analyzed the rheological properties of asphalt binder through rotational viscosity (RV), bending beam rheometer (BMR) and dynamic shear rheometer (DSR) test. Therefore, the improvement in properties of the asphalt help in improving the behavior of asphalt. The roadways and highways constructed through modified asphalts perform better and have an efficient in-service life. This reduces the vulnerability of the pavement from more frequent distresses. The study observed that less distress have less cost of maintenance and more benefits can be enjoyed from the durable pavements.

CHAPTER 3

METHODOLOGY

3.1 Experimental Design

3.1.1 Material

The base asphalt binder used in this study was 80/100 penetration grade and 80/100 modified with 5% Acrylate Styrene Acrylonitrile (ASA), while nanoparticles used in this study were Copper Oxide (CuO) and Calcium Carbonate bicarbonate ($CaCo_3$) in two different concentrations of 3% and 5% by weight of the asphalt binder. Hence, six samples were produced in the laboratory, namely; base asphalt binder, 5% ASA, 3%CuO, 5% CuO, and 3% $CaCo_3$ and 5% $CaCo_3$. The physical properties of the base asphalt and ASA polymer are listed in Table 3.1, while the physical properties of the nanoparticles are outlined in Table 3.2 and 3.3.

Table 3.1: Physical and chemical properties of asphalt cement and ASA

Material	Properties	Value
Asphalt 80/100	Specific gravity	1.03
	Penetration @ 25°C 0.1 mm	82
	Softening point ˚C Pa.s	46.0
	Viscosity @ 135 ˚C	0.24
	Ductility (cm) @ 25 ˚C Cm	≥100
	Asphaltenes (%)	12.2
	Resins (%)	30.8
	Saturates (%)	8.1
	Aromatic (%)	48.9
ASA	Size mm	5%

Specific gravity	1.04–1.07

Table 3.2: Physical and chemical properties of copper oxide nanocomposites

Material	Properties	Value
Copper Oxide nanoparticles	Formula	CuO
	Molecular Weight	6.3-6.49
	Color and Odor	Black Powder/odorless
	Form	Nano powder
	Purity	99.99%
	Average nanoparticle size (nm)	100
	Specific surface area	N/A
	Melting Point (°C)	1326
	Solubility in Water	Insoluble

Table 3.3: Physical and chemical properties of calcium carbonate nanocomposites

	Properties	Value
Calcium Carbonate nanoparticles	Formula	$CaCO_3$
	Bulk Density (g/cm^3)	0.68
	Average nanoparticle size	15˜40
	Specific surface area (m^2/g)	24 ˜32
	Crystallographic Structure	

3.1.2 Sample preparation

The samples were produced using the melt-blending technique, the asphalt was heated till became fluid at 140–150°C. The nanoparticles were added gradually in the base asphalt binder with concentrations of 3 and 5% for both modifiers at a constant temperature of 170 ± 1°C using mechanical shear mixer at a speed of 3000rpm for 60 minutes. The flowchart of the study is shown in Figure 3.1.

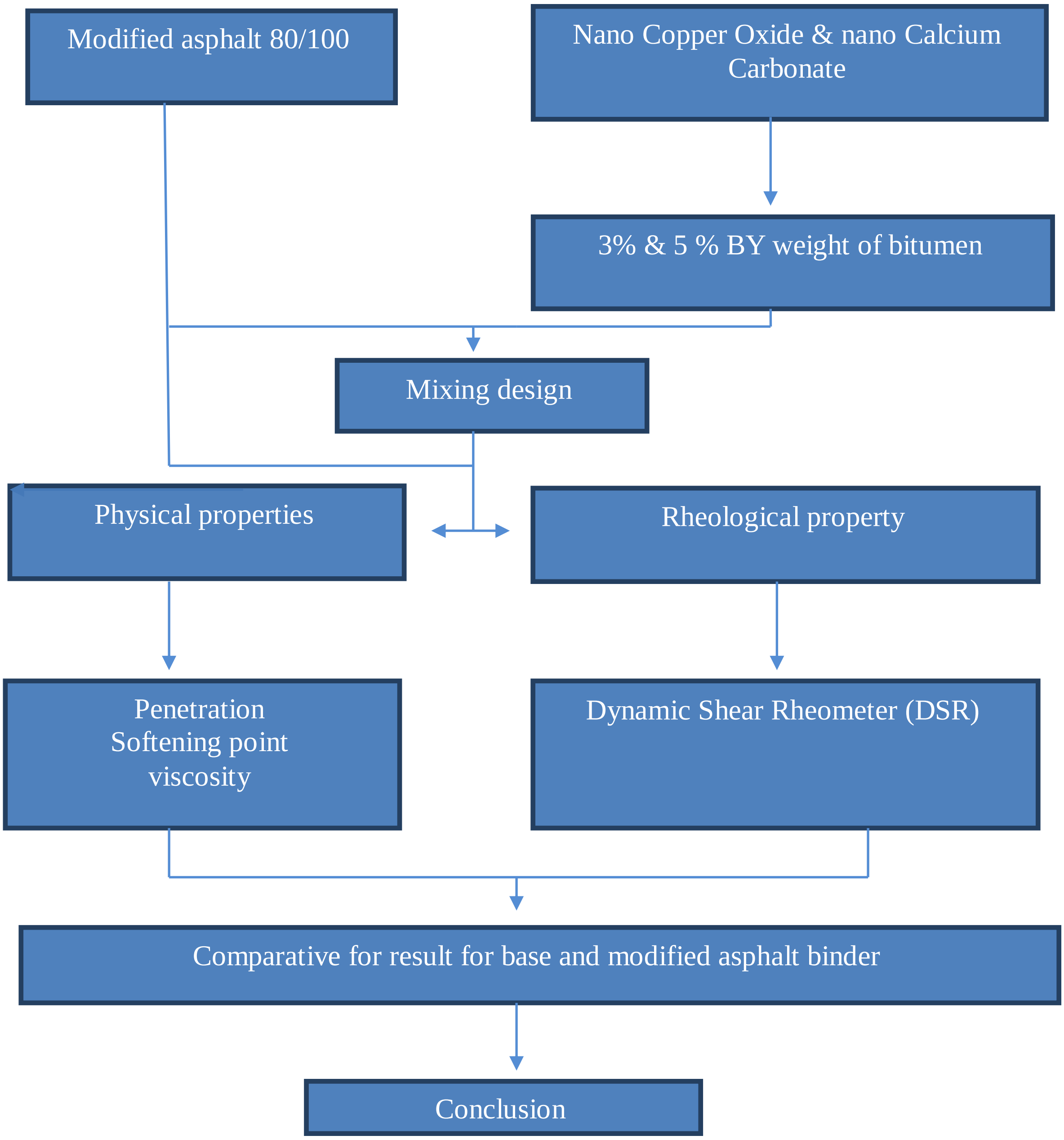


Figure 3.1 Flowchart of the study

3.2 Experimental Procedures

3.2.1 Physical properties

The physical properties of the asphalt binders used in the study were tested based on the American Society for Testing and Materials (ASTM) specifications through conventional tests like penetration test (ASTM D5), Softening Point (ASTM D36) and viscosity to evaluate the differences between the base and the modified asphalt binders. Test was also conducted to obtain the damage tolerance of the asphalt binders.

3.2.2 Penetration test

The study conducted the penetration test to measure the consistency of the sample that is being expressed in the tenths of a millimetre (dmm). This is the penetration at which the standard needle can penetrates into the sample vertically under the loading, time, and the temperature. The common penetration conditions are observed as 100g penetration for a time of 5 seconds and at the temperature of 25°C. Hence, high values for the penetration point towards the softer consistency of the asphalt binder. The penetration test can be conducted for solid and/or semi-solid bitumen. For this study, solid bitumen was used to conduct the test. The sample is prepared by heating asphalt binder until it becomes fluid. The temperature for the preparation of the sample can only be raised up to 90°C. The time required by the sample to become fluid depends on the size of the sample to be tested, the temperature of the oven and the stiffness of the binder. The test is conducted by placing the container in the oven that maintained a constant temperature of nearly 160°C. The sample should be stirred periodically until it becomes fluid. The sample becomes sufficiently fluid after an hour as stirred thoroughly and is removed from the oven. A sufficient amount of sample is taken then for the testing. When the sample is taken out of the oven, the sample temperature is maximum 60°C. This temperature is above the expected softening point. The pentrometer and bitumen sample is shown in Figure 3.2.

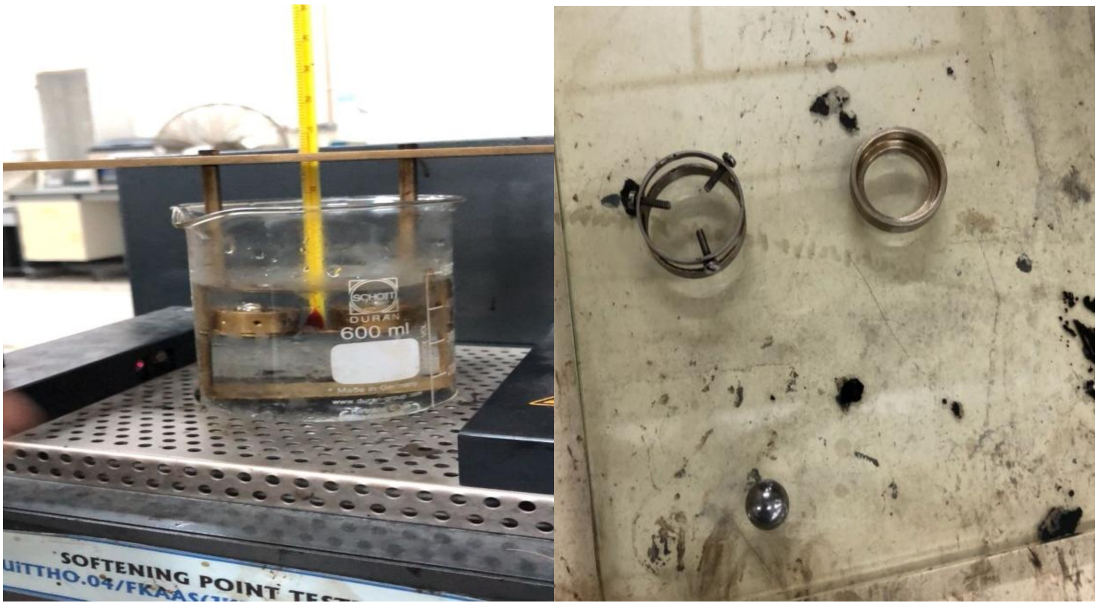
According to ASTM D5, there is not maximum limit for the time at which the sample is to be heated and/or the oven temperature. However, there is a possibility for the ageing of the binder at the time of heating. Therefore, observing the variation in the heating time for observing the variation in the penetration is effective. Thus, to determine the effect of heating time on the binder, the identical sample binders can be tested with different temperatures. To specify this variation, the identical binder samples tested with two different temperatures of 45°C and 90°C outlined that there is a negligible impact of heating temperature on the penetration of the samples (O'Connell, Mturi, & Maina, 2011).

(a) **(b)**

Figure 3.2: (a) Penetrometer (b) Fluid sample of bitumen

3.2.3 Softening point

The softening point test is conducted to observe the temperature at which the asphalt binder can be softened. This is one of the important physical properties that can be used to determine the performance of the asphalt pavement. The softening point test is conducted by the ring and ball apparatus as shown in Figure 3.3.



(a) **(b)**

Figure 3.3: Ring and ball apparatus for softening point test

The sample for testing the softening point test is prepared by heating the sample material with the temperature between 75-100°C above the softening point. The sample is stirred until it becomes fluid. It is important to make sure that the mixture has no water and/or bubbles in it. The steel rings are heated before equal to the temperature of the molten material that is placed on the metal plate which is coated with glycerin and dextrin in equal quantity. The material is levelled in the ring by removing the extra material with the help of a hot and sharp knife after it cools down for a time of 30 minutes in the air. The rings are placed in the container filled with distilled water approximately height of 50mm. The water level should be above the surface of the steel rings and the initial temperature should be 5°C. The bath is then to be heated and to raise the temperature at a uniform rate that is 5±0.5°C per minute; the liquid must be stirred consistently.

Figure 3.4: Sinking balls as temperature rises

The balls start to sink as the bitumen softens with the increase in temperature as shown in Figure 3.4. The temperature is recorded at which each of the steel balls touches the steel plate at the bottom is recorded and the average temperature close to 0.5°C is said to be the softening point. It is important to use only distilled water for heating the bitumen and the apparatus was fixed (Mettler-Toledo, 2015).

3.2.4 Rotational viscosity

The Brookfield viscometer in Figure 3.5 used to measure the rotational viscosity of the samples according to ASTM D4402 and AASHTO T316 standards. The viscosity of the samples was obtained with rotating of a spindle 21 with a speed of 20 rpm. The approximate 10.5 g of asphalt binder is used to assess the viscosity of samples. The viscosity of the base and modified binders were tested under different two temperatures (135 °C and 165°C) the readings were taken every 20 minutes. In addition, three reading were noted and the average was considered as the final results of the test.

Figure 3.5: Brookfield viscometer

3.3 Dynamic Shear Rheometer

The dynamic shear rheometer (DSR) is used to determine the rheological properties of the bitumen shown in Figure 3.6. The DSR machine is used to characterize the viscoelastic behavior of asphalt binders. This viscoelastic behavior can be evaluated at an elevated temperature. The shear modulus G* and phase angle δ of the specimen are obtained through the DSR to evaluate the viscoelastic properties. The DSR used in this study is the Rheometer HAAKE RheoStress 600. The frequency sweep was applied for 0.1 and 10 rad and the temperature sweep ranged from 46°C to 82°C. The lower plate of the DSR was warmed to develop a strong bond with the asphalt binder. The gap between the plate and the asphalt binder was ensured to be 50μm stretched more than the targeted gap (Al-Mansob R. A., et al., 2017). The study also conducted the frequency sweeps foe all binders using a plate of 25 mm in diameter and a gap of 1000 lm for medium to high temperatures including 46, 52, 58, 64, 70, 76, and 82°C. The binders were test at nine frequencies including 1 rad and to 10 rad. Super pave was used to determine the failure temperatures of the binders. The value of G*/sin δ was specified to less than 1.0 kPa. The master curves for all unmodified and modified asphalt binders were plotted using complex modulus G* and phase angle δ. The master curves are plotted at the reference temperature T_{ref} which is the relation between the stiffness and frequency. The master curve is drawn by the help of various curves at changing frequencies and temperatures through shifting parameters (Ali, et al., 2015).

Figure 3.6: Dynamic shear rheometer (DSR)

The DSR used two plates, the spindle with 8mm has a 2 mm gap and the other spindle with a 25mm diameter has a gap of 1mm. The spindle with 8mm diameter was used for low-temperatures range while 25 mm spindle was used for high-temperatures as shown in Figure 3.6.

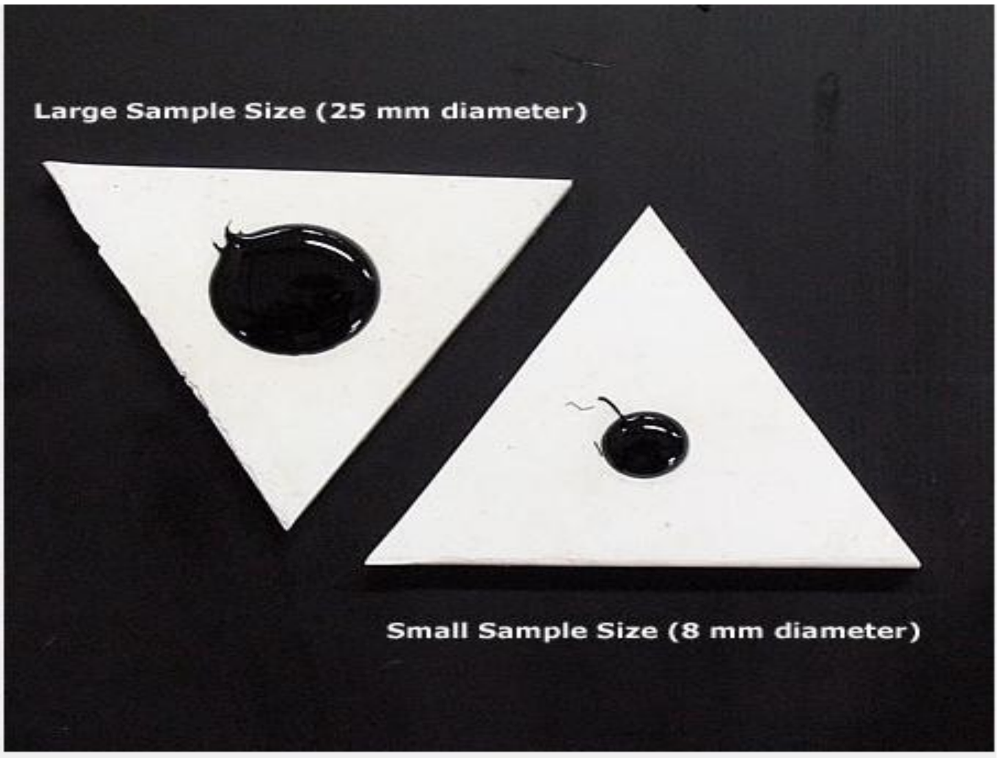


Figure 3.7: DSR sample sizes

Lastly, the target gap is adjusted, and the selected strain has to be the smallest as possible. The smallest strain will ensure measurements for the linear area. The measurement of rheological properties of the asphalt through DSR is determined Complex Shear Modulus and Phase Angle (Al-Mansob R. A., et al., 2014).

3.3.1 Complex shear modulus

The complex shear modulus is the total resistance of the sample asphalt binder against deformation. It was obtained through repeated shearing load. The complex shear modulus is a viscoelastic property of a material that is evaluated as a ratio of stress to strain when the load is applied parallel to one of two sides of the specimen whereas, the opposite side is held as fixed by another force.

3.3.2 Phase angle

The phase angle δ is defined as the lag between the shear stress applied and the shear strain obtained as a result. The asphalt binders with large phase angle are more viscous in nature. The phase angle as following limits:

- Purely elastic material: δ = 0 degrees
- Purely viscous material: δ = 90 degrees

The complex shear modulus and the phase angles are used to predict the rutting and fatigue cracking of the HMA layer. The initial concern in the pavement durability is the rutting that is often experienced earlier than fatigue cracking (Ali, et al., 2015).

The asphalt binder is said to be durable if it has enough elasticity to resist fatigue cracking. This means that it should be capable of dispersing the energy to avoid fatigue cracking for long time durability. However, it should not be too stiff because stiffer materials can also be cracked easily. Though, it must be noted that the relationship between the viscous portion and cracking is weaker than its relation to rutting (Ali, et al., 2015).

3.3.3 Isochronal plot

The isochronal plot is a curve that represents the behavior of a material at a constant frequency and/or the constant loading time. The DSR plots this graph by taking Complex Shear Modulus G* on the y-axis and temperature on the x-axis at a constant frequency. For this study, the frequency was ranged from 1 to 100 rad and the isochronal plot was graphed for 1 and 10 rad.

3.3.4 Rheological master curve

The master curve is plotted on the log-log scale. The mechanical data, G*, and the phase angle versus frequency and different temperatures are plotted as a master curve. For master curves, a reference temperature is selected initially and the values are plotted. Later, all temperature data lines are shifted to the reference temperature line horizontally to obtain a single smooth line. This shifting of data lines was done by using numerical method for shifting parameters that are different for each selected temperature. The reference temperature in this study was 52°C.

3.3.5 Black diagram

The magnitude of the complex shear modulus G* versus phase angle δ is plotted on the graph that are obtained from the dynamic test conducted by DSR. The black diagram graph only represents the dynamic data and it does not include frequency and temperature. There are two curves on the black diagram graph. The time-temperature equivalency is represented by the smooth curve while the breakdown of TTSP data and the presence of asphalt bitumen, modified bitumen and or high wax content bitumen (Al-Mansob R. A., et al., 2014).

3.3.6 Parameters of rutting

The rutting parameter is determined by dividing complex modulus G* to sin of phase angle δ (G*/Sin δ). According to Superpave the minimum value of rutting parameter must be 1 kPa at 76 °C (Al-Mansob R. A., et al., 2014).

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter discusses the results and findings of the study. The chapter highlights the change in physical properties of the asphalt binder through penetration test, softening point test, rotational viscosity and the results of rheological properties tested through dynamic shear rheometer.

4.2 Physical Properties

The physical properties of the asphalt binders were observed to be influenced when modified with 5% ASA. The physical properties of the ASA-modified asphalt further changed with the addition of 3% and 5% of CuO and $CaCO_3$. The penetration and softening point of the asphalt binder modified with ASA, CuO and $CaCO_3$ can be seen in Table 4.1.

Table 4.1: Physical properties of ASA-modified asphalt binder

Binder Type	Penetration @ 25°C	Softening Point (°C)	Viscosity at 135°C	Viscosity at 165°C
0%	82	46	0.42	0.12
3% CuO	66.4	56	0.57	0.16
5% CuO	69.1	55	0.72	0.20
3% $CaCO_3$	75.3	55	0.51	0.16
5% $CaCO_3$	76.9	53	0.61	0.20

The penetration of modified asphalt binders was decreased with the additional increase of CuO content. However, the penetration for 3% CuO was observed to be substantially less than 5% CuO with a penetration value of 66.6 followed by 5% CuO as 69.1 and the base asphalt binder has the highest penetration value as expected. Meanwhile, the penetration values for 3 and 5% $CaCO_3$ were observed to be greater than samples modified with CuO, with 75.3 and 76.9 respectively. Also, it was noted that the modified binders have the softening point higher than base asphalt binder. Moreover, the softening point of 3% CuO increased to 56°C and with 5% decreased to 55°C. The softening point for 3% and 5% $CaCO_3$ was close to CuO as 55°C and 53°C respectively.

The decreased penetration value and the increased softening point indicates the increase in the specimen stiffness and reduction of the temperature susceptibility, which means better resistance to rutting at elevated temperatures (Golestani, Nam, Nejad, & Fallah, 2015). This results was also observed when nano aluminum oxide used to modify asphalt binders (Ali, et al., 2015; Ali, Ismail, AlMansob, & Alhmali, 2017).

4.3 Rotational Viscosity

The viscosity is represents the ability of asphalt to flow and it is an important element that determines the compaction and mixing temperatures. The highest values of viscosity result in higher mixing and compaction temperatures. From Figure 4.1 it's noted that the viscosity decreases significantly and immediately with an increase in the test temperature. The viscosity of the specimen decreases substantially at high temperature. Hence, the results outline that 5% CuO has the highest mixing and compaction temperatures among the blends while the base asphalt has the lowest ranges. In addition, all modified binders have passed the requirements of Superpave standard which lees 3 Pa.s at 135 °C.

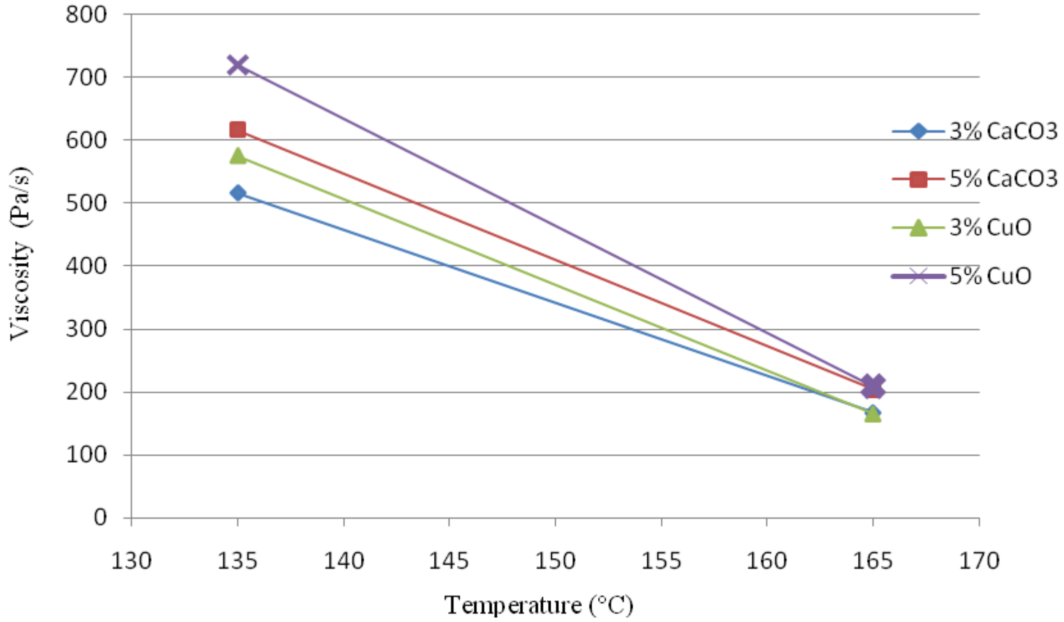


Figure 4.1: Rotational viscosity at 135°C and 165°C

4.4 Rheological Properties

4.4.1 Isochronal plot

The viscoelastic properties of the asphalt binders obtained by DSR were represented using isochronal plot. The isochronal plot represents two viscoelastic variables, complex modulus on the y-axis and temperature on x-axis. Thus, the viscoelastic behaviour of the asphalt binder can be demonstrated using isochronal plot at constant frequency with a variety of changing temperature. The isochronal plots are beneficent for comparing the complex modulus and/or phase angle of the asphalt binder at varying temperatures to best performance of modified asphalt binder compared with base asphalt binder. In addition, the temperature susceptibility of the asphalt binders can also be observed by plotting an isochronal graph. The study observed the viscoelastic behaviour of asphalt binder at two frequencies, 1 rad (0,159 Hz) as shown in Figure 4.2 and 10 rad (1.59 Hz) as shown in Figure 4.3.

The complex modulus G* for the CuO and $CaCO_3$ ASA-modified asphalt binders is observed to be higher than the base asphalt. However, the strongest complex modulus G* is observed to be for 3% $CaCO_3$. It is noticeable that the complex modulus is higher at higher temperature and greater frequency. This means that the addition of CuO and $CaCO_3$ nanocomposites to the ASA modified asphalt binder has experienced consistent increase in G* as compared to the base asphalt. Therefore, the temperature susceptibility of the modified asphalt binder is much improved at higher frequency and elevated temperature in comparison to the base asphalt. Following 3% $CaCO_3$, 3% CuO also outlined improved viscoelastic properties with better temperature susceptibility for longer durability. The results of the study are in collaboration with the studies previously done that evaluated the performance of nano-clay modified asphalt binders (Jahromi & Khodaii, 2009). The complex modulus G* of asphalt binder increase at low frequency and low temperatures but they are observed to increase more rapidly at high frequency and temperatures for the modified asphalt binders with Nano-clay and Nano-silica (Ezzat, El-Badawy, Zaki, & Breakah, 2016).

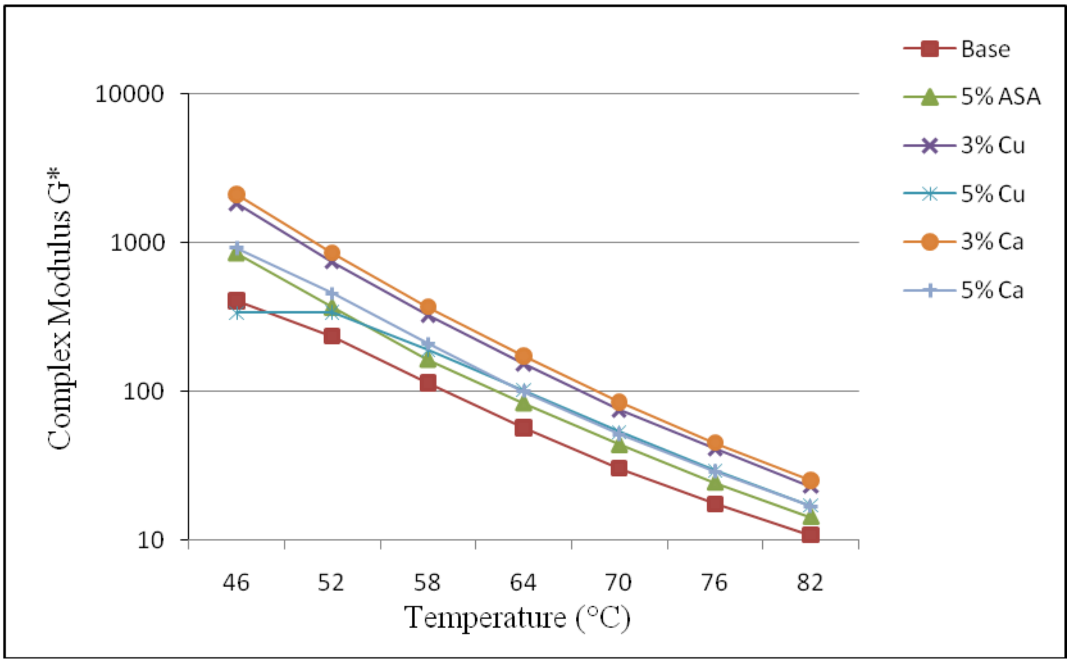


Figure 4.2: Isochronal plot of the complex modulus G* at 1 Rad

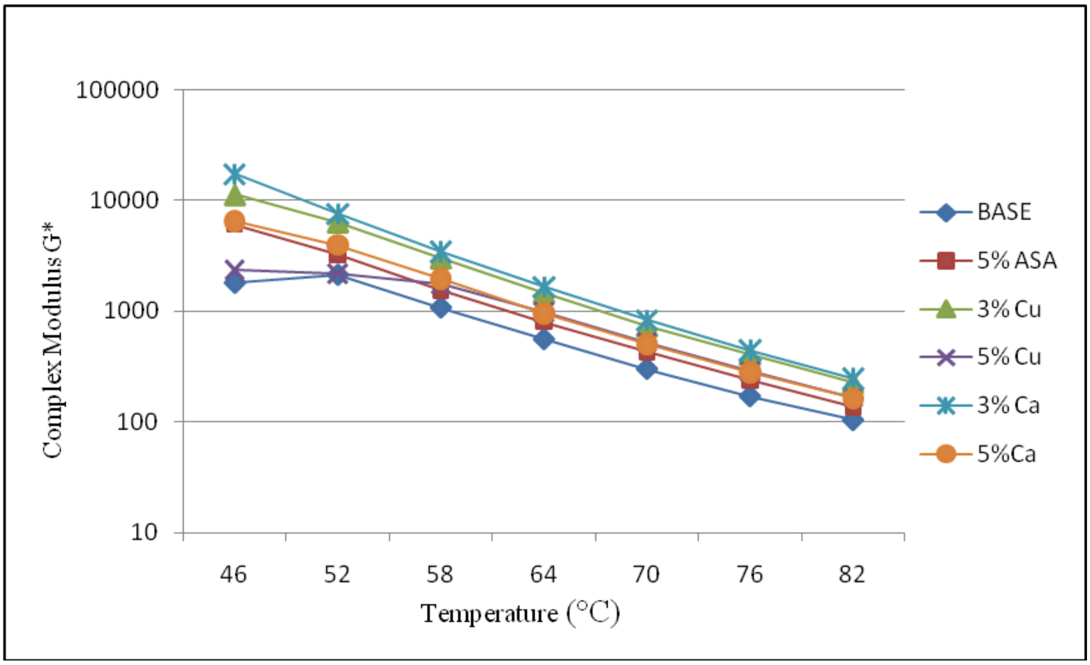


Figure 4.3: Isochronal plot of the complex modulus G* at 10 Rad

4.4.2 Rheological Master Curves

The rheological master curves are used to represent the rheological behavior of the asphalt binders. The rheological measurements are plotted on the graph including complex modulus, phase angle at different temperatures and frequencies. In this study, Figure 4.4 show that there is a consistent and smooth increase in the complex modulus of the modified asphalt binders compared to the base asphalt binder. However, 3% $CaCO_3$ and following 3% CuO for both modifiers show the best performance of asphalt binder. This means that the rheological properties of the ASA-modified asphalt with 3% $CaCO_3$ exhibit the highest resistance to permanent deformation. It is also indicates that the $CaCO_3$ nanoparticles have more strength effects on base asphalt compared with CuO nanoparticles. This it might related to chemical interaction between nanoparticles and base asphalt binder. The similar results were observed for asphalt binders modified with Calcium Carbonate Hydroxide Ca(OH)2 that significantly improved the physical and rheological properties of asphalt binders when added in different concentrations (Khodary, El-sadek, & El-Sheshtawy, 2015). Furthermore, the rheological properties of the asphalt binders modified with SiO_2 and TiO_2 were witnessed to have better rheological properties in comparison to the base asphalt (Nejad, Nazari, Naderi, Khosroshahi, & Oskuei, 2017).

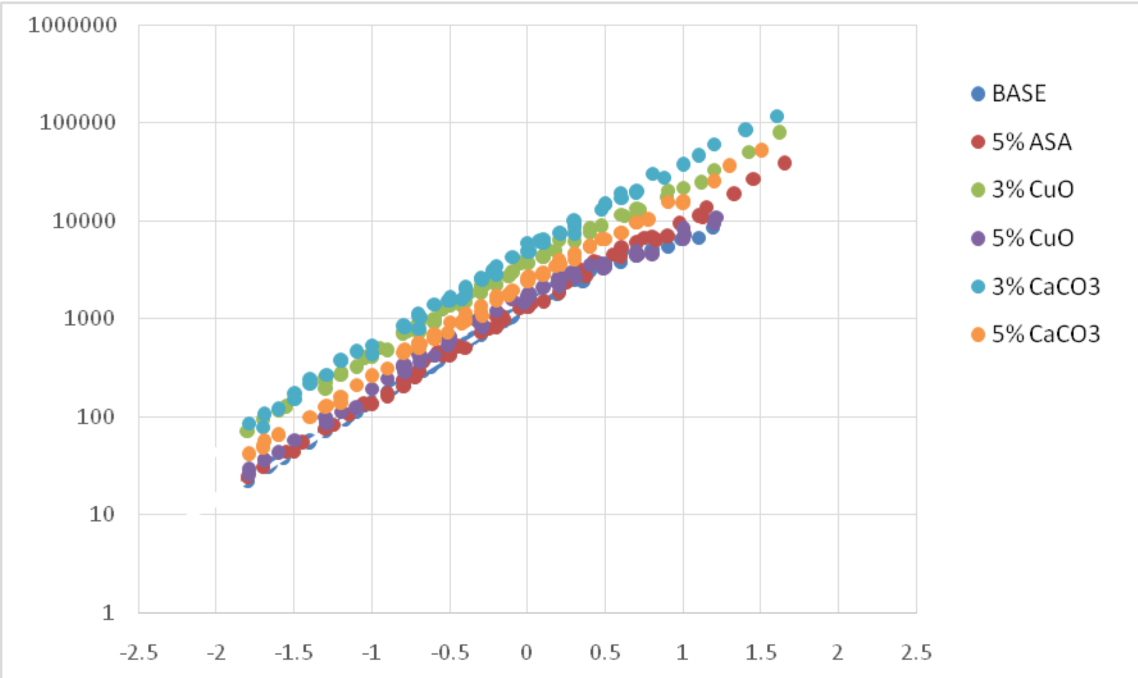


Figure 4.4: Complex modulus master curve for base and modified asphalt at the reference temperature of 52°C

4.4.3 Black diagram

The black diagram is the representation of varying temperatures and frequencies plotted as complex modulus versus phase angle values obtained from the dynamic shear rheometer tests. The black diagram is used to highlight the elastic behavior of the base and modified asphalt binders. The black diagram can experience deviations due to changing structure of the bitumen, variations in the bitumen composition, and the unavoidable measurement errors. Figure 4.5 outlines the highest value of complex modulus G* at a low phase angle for ASA-modified asphalt binder with 3% $CaCO_3$, following by 3% CuO. This means that 3% of both modifiers have the highest viscoelastic properties as compared to control asphalt which indicate highest resistance to rutting at high temperatures (Al-Mansob R. A., et al., 2014).

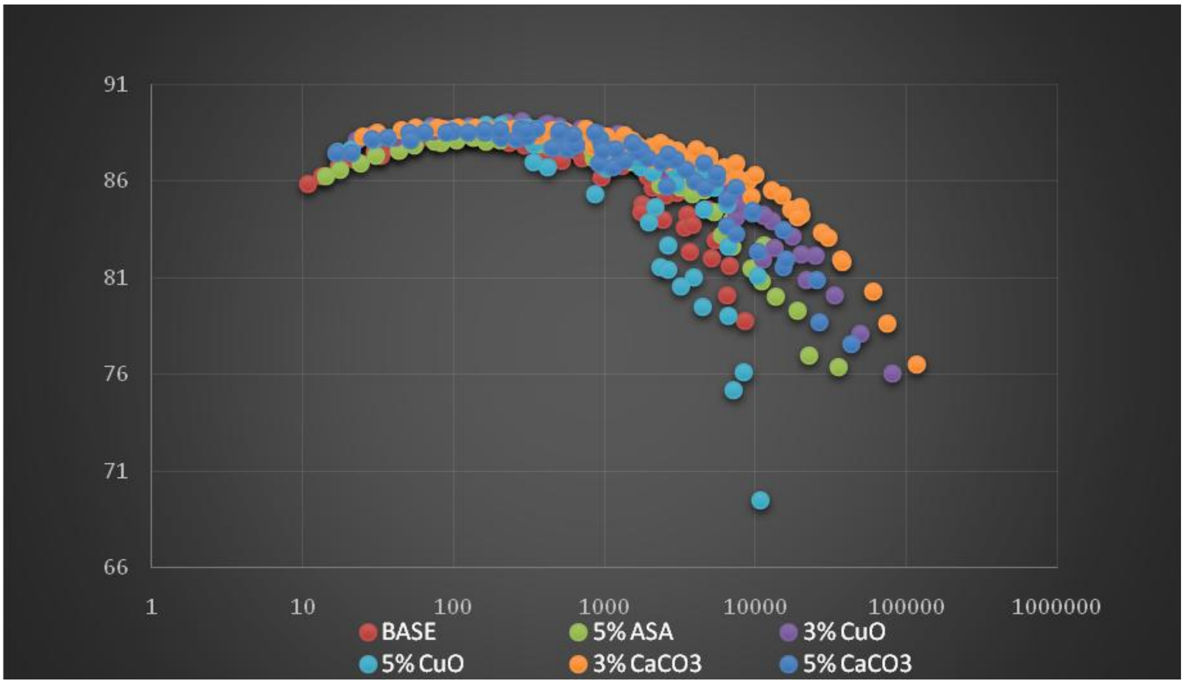


Figure 4.5: Black diagram for unmodified and modified asphalt binders

4.4.4 Fail temperature

The fail temperature is one of the important rheological measurements of asphalt binder as it's the temperature at which ratio of complex modulus G*/sin δ is less than 1.0 kPa. The failure temperature is used to determine the performance grade of the asphalt binders. The obtained the failure temperatures were greater than 58 °C and less than 69 °C as shown in Figure 4.6. Moreover, with additional increase of modifiers content the failure temperatures were improved around 6.9% for modified asphalt binders with ASA, 15.52% for 3% CuO, 10.34%for 5% CuO, 18.97% for 3% $CaCO_3$ and followed by 10.34% 5% $CaCO_3$. The studies revealed that the modified asphalt binders have comparatively high fail temperatures than the control asphalt especially for 3% $CaCO_3$. That means the nanoparticles has ability to increase the performance grade of base asphalt binder and reduced the permanent deformation effects.

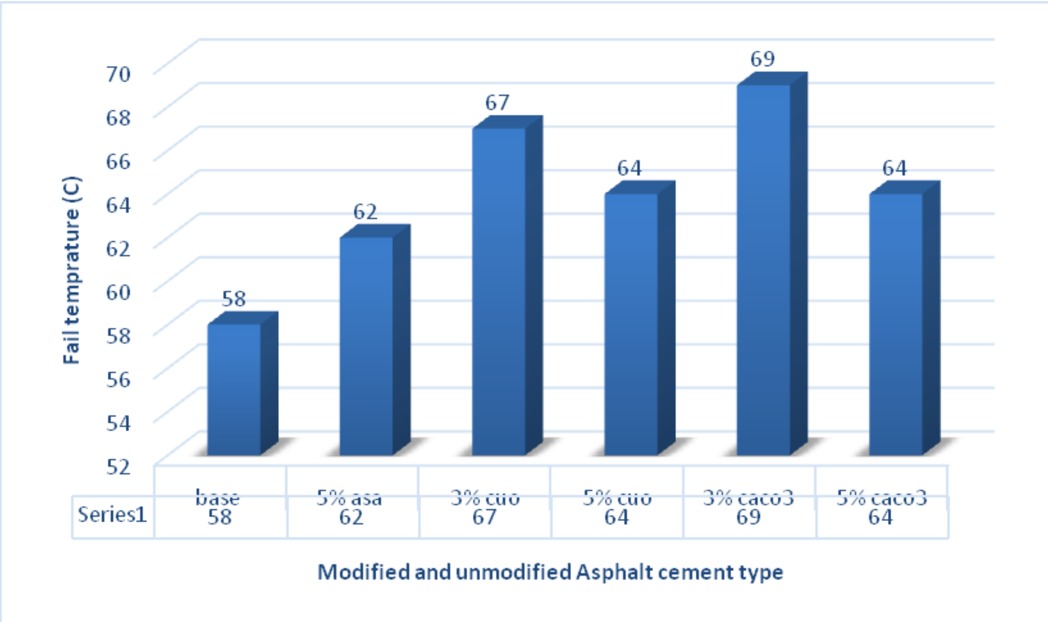


Figure 40.6: Fail temperatures of modified and unmodified asphalt binders

4.4.5 Rutting parameter

The present study evaluated the resistance of base and modified asphalt binders against rutting at high temperatures using the dynamic shear rheometer (DSR). The test conducted among seven varying temperatures including, 46, 52, 58, 64, 70, 76 and 82°C on constant loading frequency of 10 rad (1.59 Hz). The rutting parameter is defined as the ratio of G*/sin δ which is the resistance of the asphalt binder to rutting at high temperatures. The rutting parameter for the base and modified asphalt binders is presented in Figure 4.7. The modified asphalt with 3% $CaCO_3$ observed to have highest rutting parameter following by 3% CuO. Meanwhile, modified blends with 5% CuO and 5% $CaCO_3$ have the lowest rutting value compared to samples modified with 3% $CaCO_{3,}$ but still better than base asphalt cement. This means that the rutting resistance is improved among the modified asphalt binders than the control asphalt. The higher rutting parameters indicate highest resistance to deformation for better durability and high performance. In comparison, 5% CuO observed to have slightly different behaviour as it tends to decrease may be because of specimen incompatibility with the modifiers. Nevertheless, the rutting parameter values for all the modified binders observed to be greater than 1.0 kPa at approximately 60°C as shown in Figure 4.7. Similar results were observed with ASA modified asphalt binders with SBS and SBS/nano-clay (Pamplona, et al., 2012).

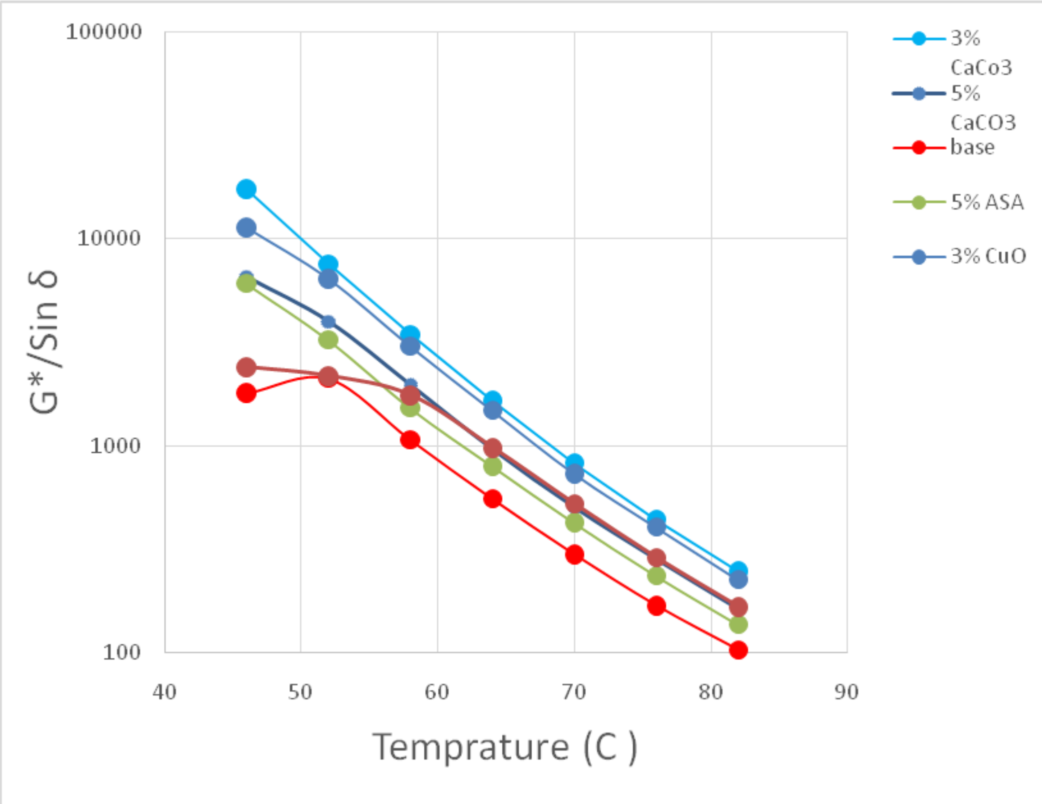


Figure 4.7: Effect of temperature on rutting parameter of base and modified asphalt binders

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Introduction

Asphalt is the filtrate of the petroleum refiners that is seen as a cost-effective, convenient and a simple way to utilize the petroleum residual material from the refining. The asphalt binders are perceived as a value-added product that has a high level of production flexibility in the pavement. In the recent years, the performance of asphalt binders is improved by modification with nanocomposites to achieve enhanced properties and ensure quality in service delivery. The performance of asphalt binders modified with nanocomposites as compared to the base asphalt binders is observed as remarkable. The nanocomposite asphalt binders are more resilient to deformation. The performance of asphalt binders is affected at high and/or low temperature as a result of rutting and fatigue cracking. The improvement in the physical and rheological properties of the asphalt binders with nanocomposites improves the performance and durability of the asphalt pavements.

There is a consistent research in the development and production of asphalt material that is more resilient and capable to resist deformation at high and low temperature. The improvement in nanotechnology is obvious for the nanocomposites that are popularly used in enhancing the properties of the asphalts. The modified asphalt materials are more resilient to temperature susceptibility. There are different factors including, aging, moisture susceptibility, and or aggregate grade that can substantially affect the performance and durability of the asphalt roadways. Therefore, the asphalt pavements are challenged despite being cost-effective and more durable than the concretes.
The development of technology has developed technologies and methods for testing the reliability of the asphalt binders. The reliability of the asphalt binders can be tested through their physical properties by testing viscosity, penetration, and softening point. Dynamic Shear Rheometer (DSR) was used to determine the rheological properties of the

asphalts. The tests for checking the pavement durability are important to analyze and evaluate the change in the properties that can help in finding an optimum concentration of the modifier content. However, there are set standards for conducting the tests that are important to validate the results obtained from these tests. The standard for conducting these tests is approved by American Society for Testing and Materials (ASTM).

5.2 Conclusion

Different tests were conducted in this study to evaluate the changing in the properties of asphalt binder modified with Copper Oxide (CuO) and Calcium Carbonate ($CaCO_3$) nanocomposites. The physical rheological properties of the base and modified asphalt binders were tested using penetration, softening point, and viscosity test and Dynamic Shear Rheometer (DSR). In addition, five binders were produced in the experimental excluding base asphalt binder namely: 5% ASA modified asphalt binder, 3 and 5% $CaCO_3$, and 3% and 5% CuO. After evaluating the properties of asphalt binders the following conclusions could be made: The test was conducted by using a penetrometer and the sample was placed the container in the oven that maintained a constant temperature of nearly 160°C. The sample was stirred periodically until it became fluid. The sample became sufficiently fluid after an hour as stirred thoroughly and was removed from the oven. A sufficient amount of sample was taken then for the testing. When the sample was taken out of the oven, the sample temperature was maximum 60°C. The results of the study observed substantial changes in the values of penetration and softening point of the modified specimens. The penetration values for up to 5% ASA modified asphalt binder decreased with the addition 3% and 5% CuO. However, the penetration for 3% CuO was observed to be substantially less as 19.02% than 5% CuO as 15.73% with a penetration value of 66.4 followed by 69.1 respectively as compared to the base asphalt binder. The penetration values for 3% and 5% $CaCO_3$ were observed to be greater than the 3 and 5% CuO as 75.3 and 76.9 respectively with a percentage change of 8.17% and 6.22% respectively as compared to the base asphalt binder. The softening point with 3% CuO increased to 56°C and with 5% CuO decreased to 55°C with a percentage change of 21.74% and 19.57% respectively as compared to base asphalt binder. The softening point for 3% $CaCO_3$ and 5% $CaCO_3$ was 55°C and 53°C with a percentage change of 19.57%

and 15.22% respectively as compared to base asphalt binder. Thus, it can be concluded that 3% CuO has lowest penetration with high softening point that means, it has better resistance to temperature susceptibility as compared to others. The decreased penetration values and the increased softening point indicated the increase in the specimen stiffness. This means that the increased stiffness is the increase in the penetration. The addition of nanocomposites increased the resistance against temperature susceptibility for durability of the pavement and their resistance against deformation.

The rotational viscosity of the samples was measured by the Brookfield viscometer according to ASTM D4402 and AASHTO T316 standards. The measurements were obtained by the help of a spindle 21 that has a constant speed of 20 rpm. The approximate base of asphalt cement was 10.5 g. The samples for Copper Oxide and Calcium Carbonate ASA-modified asphalt were tested. The temperature range was 135°C and 165°C within a time of 30mins. Viscosity test is among the conventional tests that determines the binder's flow and mixing temperature. The results of viscosity test outlined that the viscosity decreases significantly and immediately with an increase in the temperature of the sample specimen modified with CuO and $CaCO_3$. The high viscosity values determine high mixing temperatures. The increase in temperature significantly decreased the viscosity of all modified samples regardless of their concentration. The highest viscosity value observed in the results demonstrates high compaction and mixing temperature for ASA-modified asphalt with specifically 5% CuO and $CaCO_3$ with a percentage change of 71.43% and 45.24% respectively as compared to base.

The (DSR) determined rheological properties of the bitumen. DSR determined the viscoelastic behavior through shear modulus (G*) and the phase angle (δ) of all samples of asphalt binders. This viscoelastic behavior was evaluated at an elevated temperature to observe resistance to rutting. The DSR used in this study is the Rheometer HAAKE RheoStress 600. The frequency sweep was applied for 0.1 and 10 rad. The sweep temperature ranged from 46°C to 82°C. The isochronal plot revealed that the stiffness of the modified asphalt binders increased in comparison to the control asphalt with the increase in temperature. This complex modulus was plotted against the temperature that outlined pronounced results for increasing the hardness of the modified binder for longer durability. The complex modulus for 3% $CaCO_3$ and 3% CuO significantly increased with an increase in the temperature at varying frequencies of 1 and 10 rad. Therefore, the temperature susceptibility of the modified asphalt binder is much improved at higher frequency and elevated temperature in comparison to the base asphalt binder. Thus, the results outlined improved viscoelastic properties with increased resistance to temperature susceptibility. The master curves of all ASA-modified asphalt binders with CuO and $CaCO_3$ outlined an increasing elastic behavior. The master curves represented enhanced elasticity among the modified asphalt binders as compared to the control asphalt. It was noticeable that the rheological properties of the ASA-modified asphalt with 3% $CaCO_3$ exhibit the highest resistance to deformation. The stronger values of complex modulus outlined stronger resistance to deformation at different temperatures and with varying frequencies. Similarly, the greater fail temperature for modified asphalt binders as compared to the control asphalt outlined better resistance and high durability. In addition, the black diagram also revealed extraordinary resistance to rutting for the ASA-modified asphalt binders with CuO and $CaCO_3$ in comparison to the base. Lastly, from the results of the rutting parameter tested at a constant frequency of 10 rad (1.59 Hz), it was concluded that the ASA-modified asphalt binder with 3%$CaCO_3$ outlined remarkable resistance to rutting at high temperatures. Thus, the overall results of the study outlined that the modified asphalt binders with nanocomposites are stronger and resilient to temperature susceptibility. The modified asphalt binders are better in performance and durability as compared to the control asphalt binders. The significant improvement in physical and rheological properties of the modified binders indicated that the nanocomposite modified asphalt binders have high resistance to deformation for durable pavements at low cost for building and maintenance.

5.3 Recommendation for Future Research

The performance of the modified asphalt binders with nanocomposites of CuO and $CaCO_3$ at two different concentrations was evaluated at high temperatures. Therefore, the following recommendation will be helpful for future work:

1- It is recommended to evaluate the performance of asphalt binders modified with nanoparticles at low temperatures to find out the effect of nanoparticles against fatigue cracking.

2- To find out the main causes of increasing of the stiffness and to observe the changes in the structure of base asphalt binder, it's recommended to conduct chemical and morphology test such as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning electron microscope (SEM).

3- It recommended to evaluate the effects of ageing condition to figure out of the nanoparticles have ability to delay the ageing.

REFERENCES

Abdul-Mawjoud, A. A., & Thanoon, L. (2015). Evaluation of SBR and PS-Modified Asphalt Binders and HMA Mixtures Containing Such Binders. *Applied Research Journal, 1*(9), 460-469.

Albrka, S. I., Ismail, A., Yusoff, N. I., AlHamali, D. I., & Musbah, A. (2016). Performance Properties of ASA polymer Modified Asphalt Binders and Mixtures. *Journal of Engineering Science and Technology, 11*(8), 1155 - 1163.

Ali, S. I., Ismail, A., AlMansob, R. A., & Alhmali, D. I. (2017). Evaluation of elevated temperature properties of asphalt cement modified with aluminum oxide and Calcium Carbonate nanoparticles. *Materials Science and Engineering.* IOP.

Ali, S. I., Ismail, A., Karim, M. R., Yusoff, N. I., Al-Mansob, R. A., & Aburkaba, E. (2016). Performance evaluation of Al2O3 nanoparticlemodified modified asphalt binder. *Road Materials and Pavement Design*, 1-16.

Ali, S. I., Ismail, A., Yusoff, N. I., Karim, M. R., Al-Mansob, R. A., & Alhamali, D. I. (2015). Physical and rheological properties of acrylate–styrene–acrylonitrile modified asphalt cement. *Construction and Building Materials, 93*, 326-333.

Al-Mansob, R. A., Ismail, A., Rahmat, R. A., Borhan, M. N., Alsharef, J. M., Albrka, S. I., & Karim, M. R. (2017). Evaluation of permanent deformation and durability of epoxidized natural rubber modified asphalt mix. *Materials Science and Engineering, 236*, 1-19.

Al-Mansob, R. A., Ismail, A., Rahmat, R. A., Borhan, M. N., Alsharef, J. M., Albrka, S. I., & Karim, M. R. (2017). The performance of Epoxidised Natural Rubber modified asphalt using nan-alumina as additive. *Construction and Building Materials, 155*, 680-687.

Anderson, D., Youtcheff, Y., & Zupanick, M. (2000). *Asphalt binders.* TRB Committee on Characteristics of Bituminous Materials. TRB Millennium Paper Series.

Bayekolaei, M. D., Naderi, K., & Najad, F. M. (2017). The effects of base binder and styrene–butadiene–styrene structure on rutting resistance of polymer–nanocomposite asphalt mixture. *Journal of Elastomers and Plastics, 20*(10), 2-18.

Chen, P. E.-S., Liao, M.-C., & Shiah, M.-S. (2002). Asphalt Modified by Styrene-Butadiene-Styrene Triblock Copolymer: Morphology and Model. *Journal of Materials in Civil Engineering* , 224-228.

Delgadillo, R., Bahia, H. U., & Lakes, R. (2012). A nonlinear constitutive relationship for asphalt binders. *Materials and Structures, 45*(3), 457-470.

Domingos, M. D., & Faxina, A. L. (2013). Rheological analysis of asphalt binders modified with Elvaloy terpolymer and polyphosphoric acid on the multiple stress creep and recovery test. *Materials and Structures*, 1-11.

Ezzat, H., El-Badawy, S., Zaki, A. E.-S., & Breakah, T. (2016). Evaluation of Asphalt Binders Modified with Nanoclay and Nanosilica. *Procedia Engineering, 143*, 1260-1267.

Fini, E. H., Al-Qadi, I. L., You, Z., Zada, B., & Mills-Beale, J. (2012). Partial Replacement of Asphalt Binder with Bio-binder: Characterization and Modification. *Journal of Pavement Engineering, 13*(6), 515–522.

Franke, R., & Ksaibati, K. (2015). A methodology for cost-benefit analysis of recycled asphalt pavement (RAP) in various highway applications. *International Journal of Pavement Engineering, 16*(7), 660–666.

Hernández-Olivares, F., Witoszek-Schultz, B., Alonso-Fernández, M., & Benito-Moro, C. (2009). Rubber-modified hot-mix asphalt pavement by dry process. *International Journal of Pavement Engineering, 10*(4), 1-13.

Hiroyuki, M. (2009). Characterization of material ductility of PP/EPR/talc blend under wide range of stress triaxiality at intermediate and high strain rates. *Journal of Applied Polymer Science, 111*(2), 854-859.

Hussain, M., Ghaly, N., & Ibrahim, I. (2008). Modified Hot Mix Asphalts for Road Maintenance. *World Applied Sciences Journal, 5*(2), 236-244.

Jahromi, S. G., & Khodaii, A. (2009). Effects of nanoclay on rheological properties of bitumen binder. *Construction and Building Materials, 23*, 2894–2904.

Jasso, M., Hampl, R., Vacinb, O., Bakos, D., Stastna, J., & Zanzotto, L. (2015). Rheology of conventional asphalt modified with SBS, Elvaloy and Rheology of conventional asphalt modified with SBS, Elvaloy and. *Fuel Processing Technology, 140*, 172-179.

Katman, H. Y., Ibrahim, M. R., Karim, M. R., Koting, S., & Mashaan, N. S. (2016). Effect of Rubberized Bitumen Blending Methods on Permanent Deformation of SMA Rubberized Asphalt Mixtures. *Advances in Materials Science and Engineering*, 1-13.

Khodary, F., El-sadek, M. A., & El-Sheshtawy, H. (2015). CaO/Bitumen Nanocomposite: Synthesis and Enhancement of Stiffness Properties for Asphalt Concrete Mixtures. *International Journal of Scientific & Engineering Research, 6*(1), 444-447.

Kowalski, K. J., Król, J., Radziszewski, P., Casado, R., Blanco, V., Pérez, D., . . . Wayman, M. (2016). Eco-friendly materials for a new concept of asphalt pavement. *Transportation Research Procedia, 14*, 3582 – 3591.

Mubaraki, M., Ali, S. I., Ismail, A., & Yusoff, N. I. (2016). Rheological Evaluation of Asphalt Cements Modified With ASA Polymer and Al2O3 Nanoparticles. *Procedia Engineering, 143*, 1276–1284.

Nejad, F. M., Nazari, H., Naderi, K., Khosroshahi, F. K., & Oskuei, M. H. (2017). Thermal and rheological properties of nanoparticle modified asphalt binder at low and intermediate temperature range. *Petroleum Science and Technology, 35*(7), 641-645.

Pamplona, T. F., Amoni, B. d., Alencar, A. E., Lima, A. P., Ricardo, N. M., Soaresa, J. B., & Soares, S. d. (2012). Asphalt Binders Modified by SBS and SBS/Nanoclays:

Effect on Rheological Properties. *Journal of the Brazilian Chemical Society, 23*(4), 639-645.

Presti, D. L. (2013). Recycled Tyre Rubber Modified Bitumens for road asphalt mixtures: A literature review. *Construction and Building Materials, 49*, 863-880.

Singh, M., Kumar, P., & Maurya, M. R. (2013). Strength characteristics of SBS modified asphalt mixes with various aggregates. *Construction and Building Materials, 41*, 815-820.

Tabatabaei, S. A., Kiasat, A., & Alkouhi, F. K. (2013). The Effect of Styrene-Butadiene-Rubber (SBR) Polymer Modifier on Properties of Bitumen. *International Journal of Materials and Metallurgical Engineering, 7*(10), 785-787.

Topal, A. (2010). Evaluation of the properties and microstructure of plastomeric polymer modified bitumens. *Fuel Processing Technology, 91*, 45-51.

Updyke, P. E., & Diaz, I. (2008). California Pavement Preservation .

Wang, T., Yi, T., & Yuzhen, Z. (2010). The Compatibility of SBS-Modified Asphalt. *Petroleum Science and Technology, 28*, 764–771.

Yazdani, A., & Pourjafar, S. (2012). Optimization of Asphalt Binder Modified with PP/SBS/Nanoclay Nanocomposite using Taguchi Method. *International Journal of Materials and Metallurgical Engineering, 6*(7), 532-535.

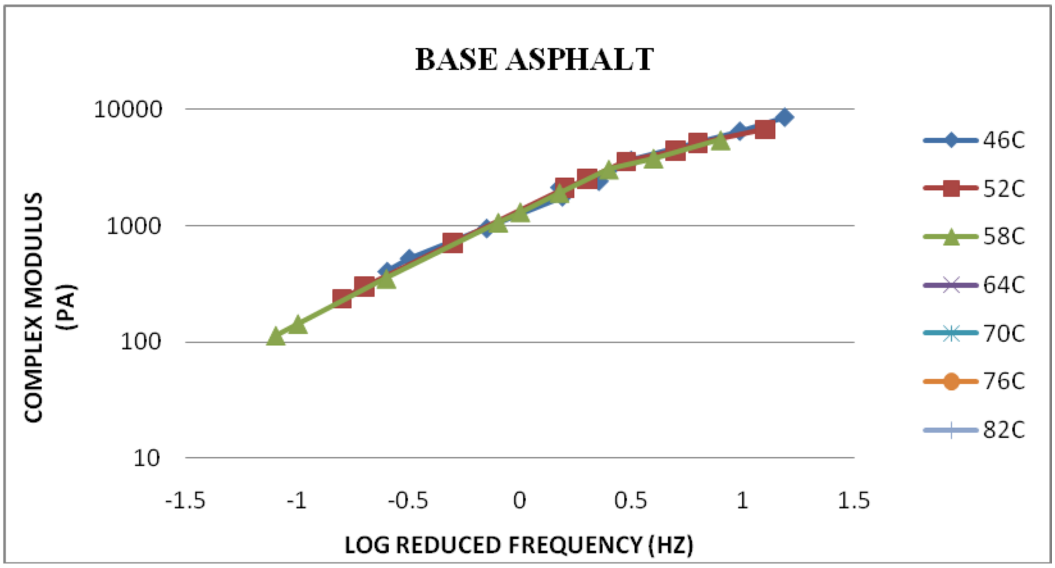
Yildirim, Y. (2007). Polymer modified asphalt binders. *Construction and Building Materials, 21*(1), 66-71.

Zhuang, C., Li, N., Zhao, W., & Cai, C. (2017). Effects of SBS Content on the Performance of Modified Asphalts. *Materials Science and Engineering, 216*

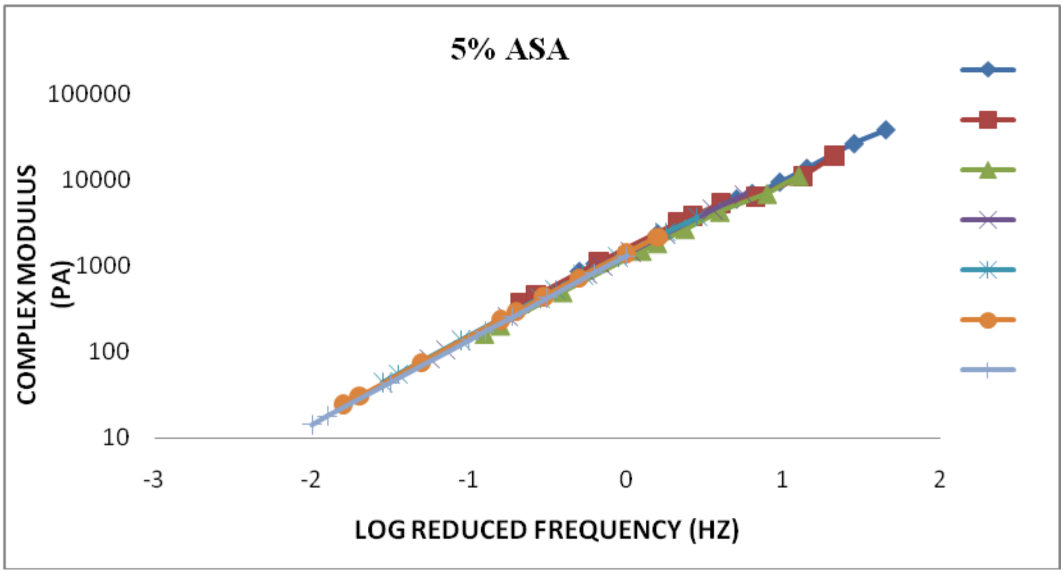
APPENDICES

APPENDIX 1:

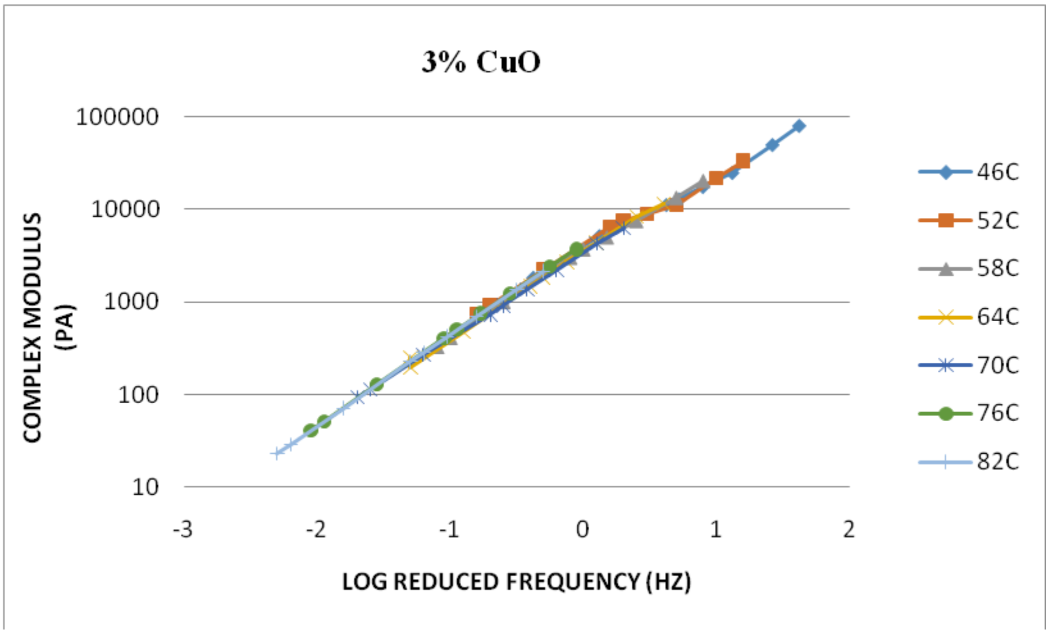
RHEOLOGICAL MASTER CURVES FOR UNMODIFIED AND MODIFIED ASPHALT



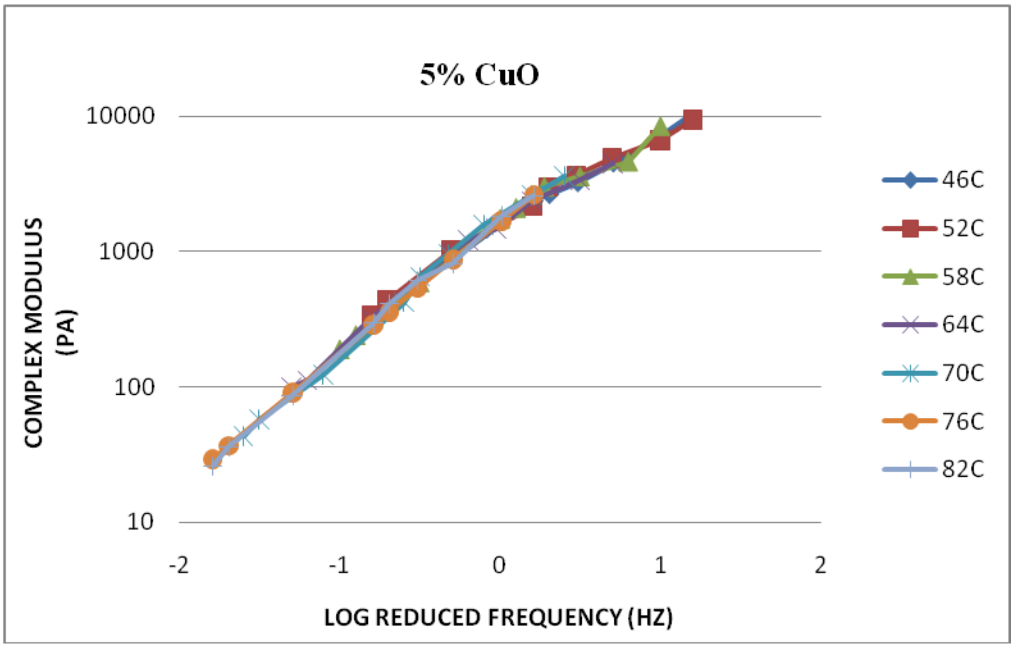
Rheological master curve for unmodified asphalt binder



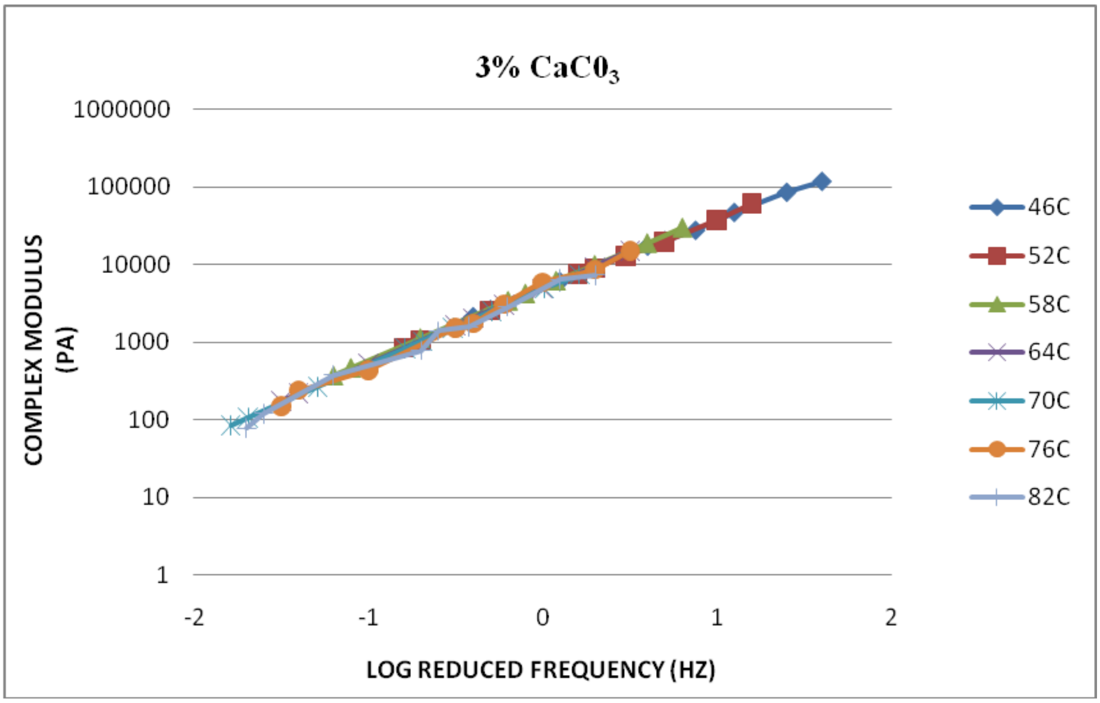
Rheological master curve for unmodified asphalt binder with 5 %ASA



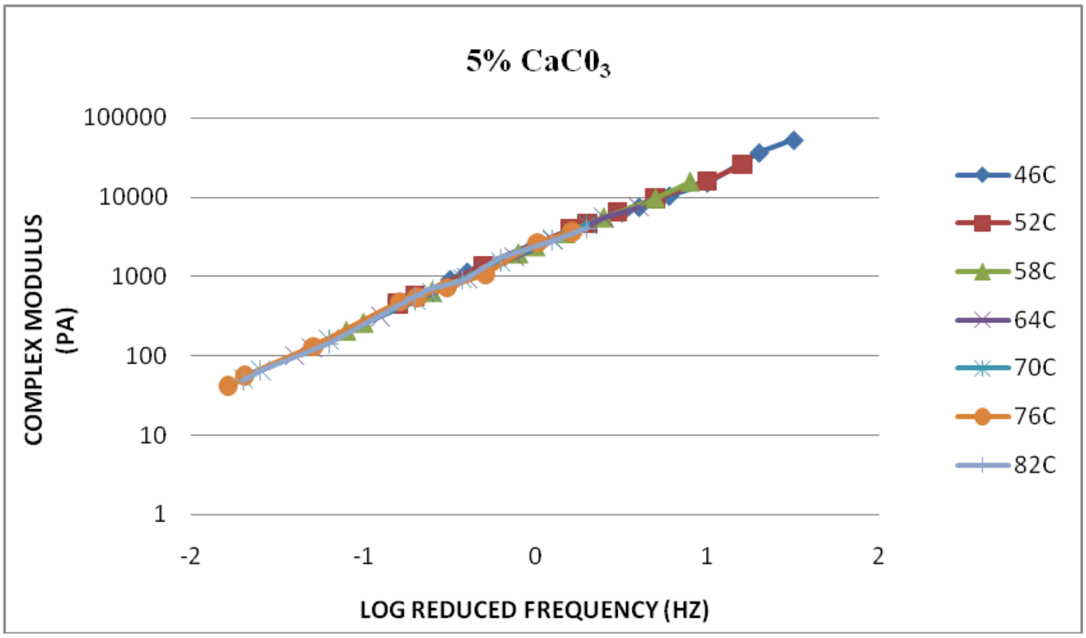
Rheological master curve for modified asphalt binders with 3% CuO



Rheological master curve for modified asphalt binders with 5% CuO



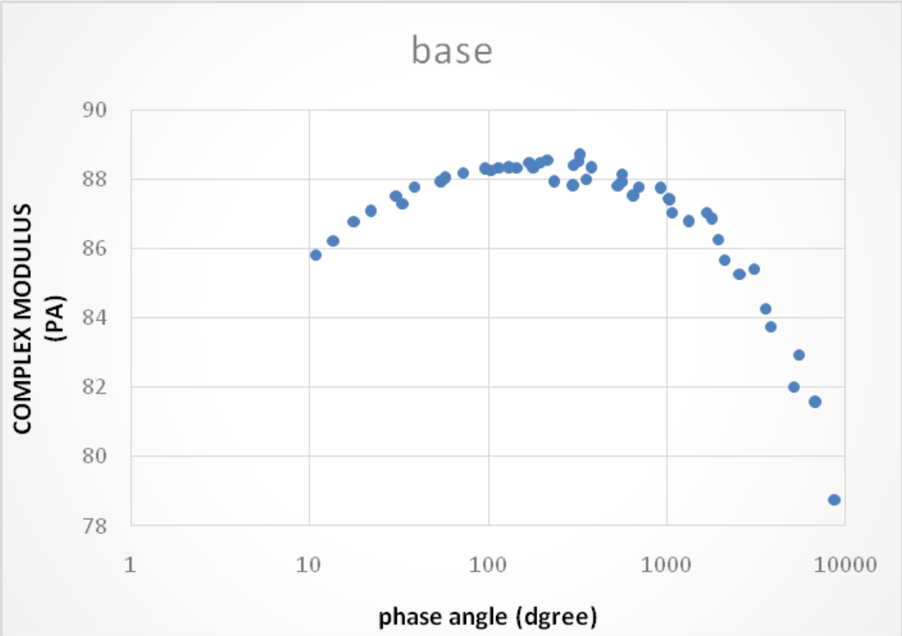
Rheological master curve for modified asphalt binders with 3% $caco_3$



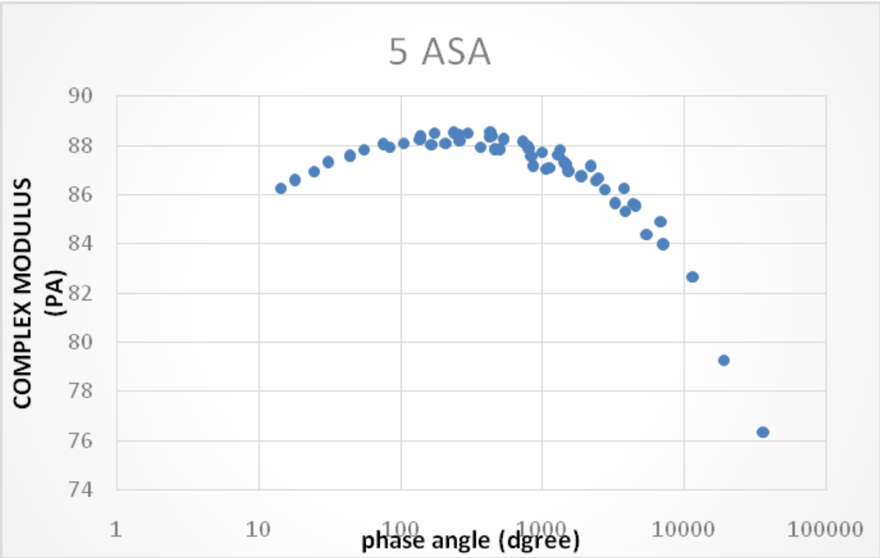
Rheological master curve for modified asphalt binders with 5% $caco_3$

APPENDIX 2:

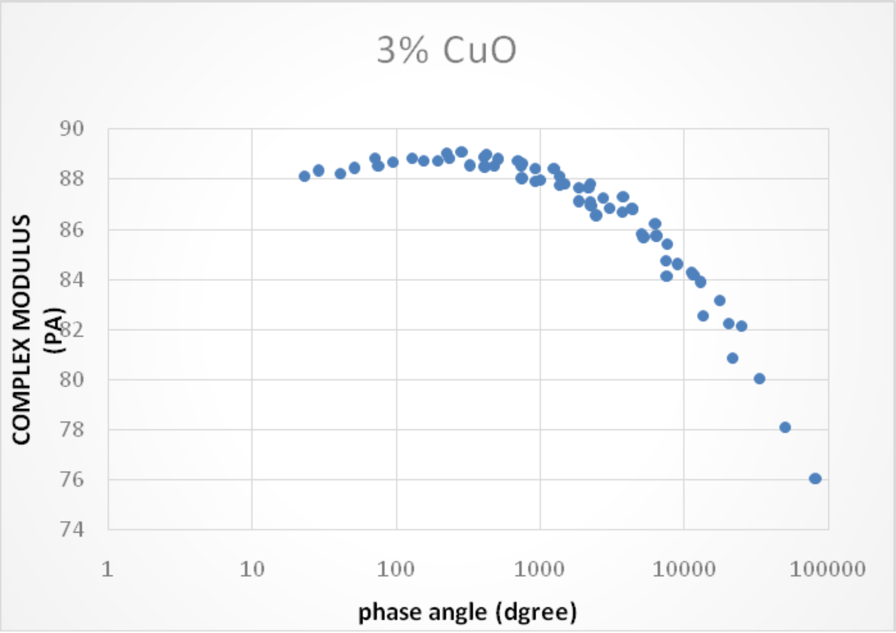
CURVES OF BLACK DIGRAM



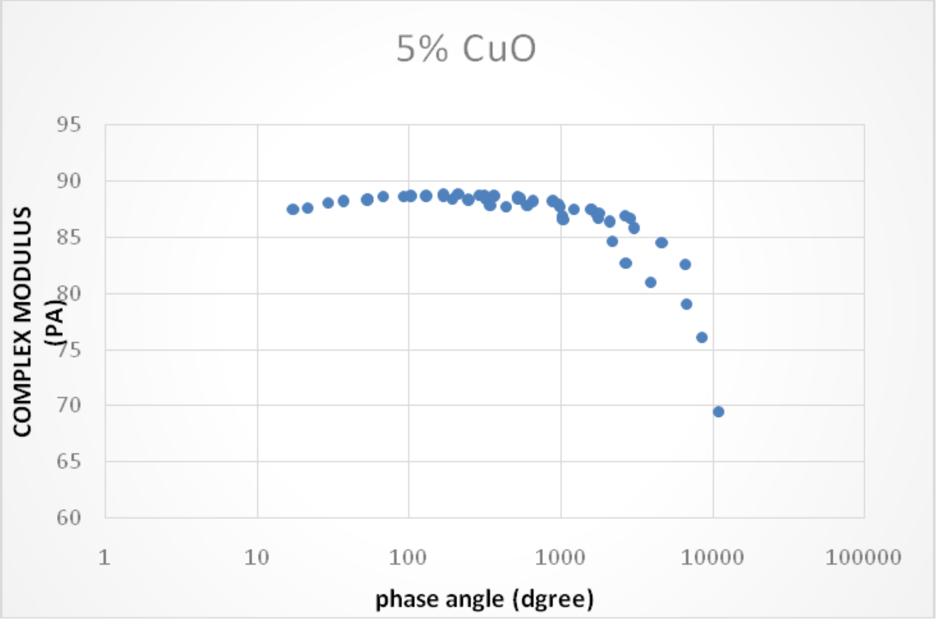
Black diagram for unmodified asphalt binders



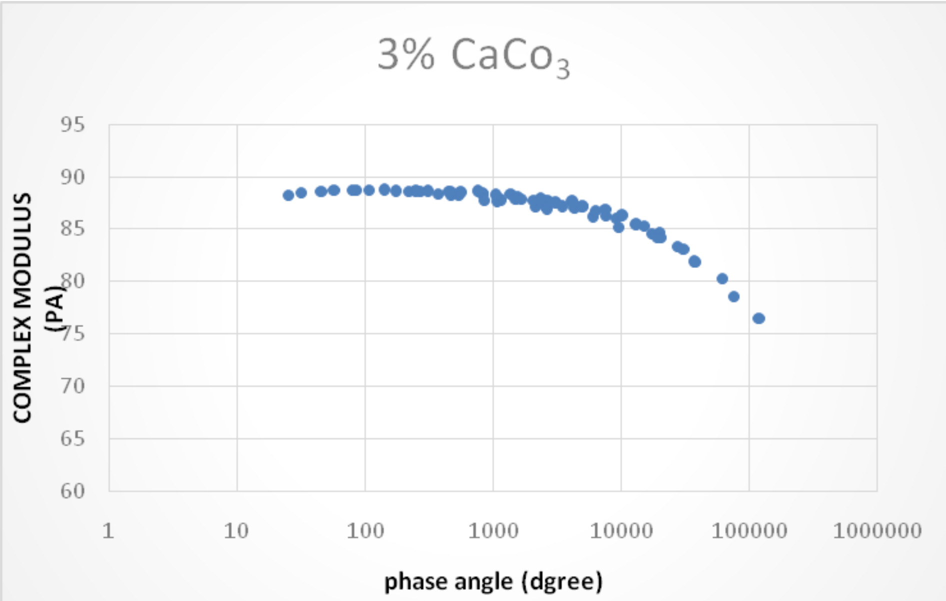
Black diagram for modified asphalt binders with % ASA



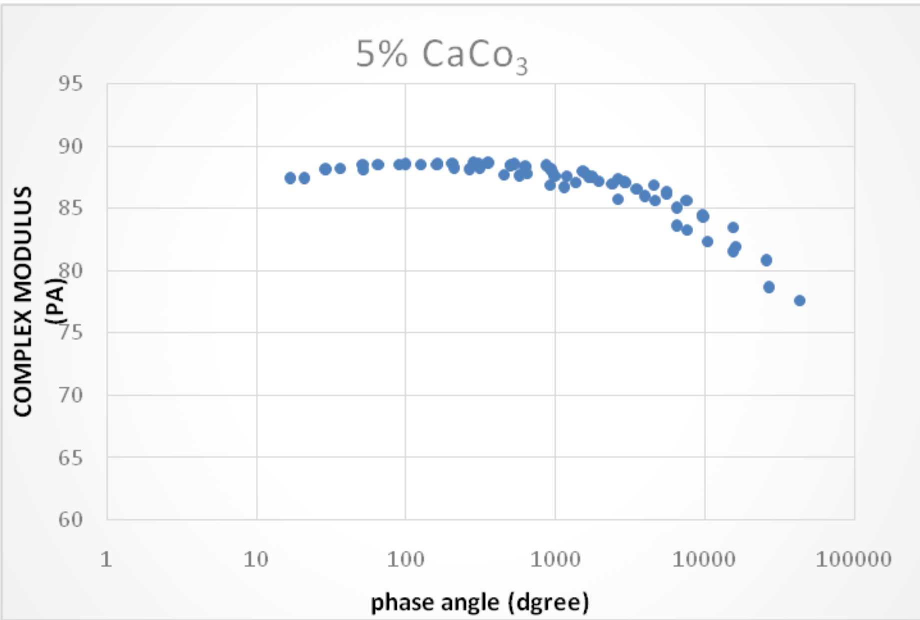
Black diagram for modified asphalt binders with 3% CuO



Black diagram for modified asphalt binders with 5% CuO



Black diagram for modified asphalt binders with 3% CaCo3



Black diagram for modified asphalt binders with 5% CaCo3

APPENDIX 3:
PENETRATION TEST

Penetration test machine

Penetration test machine

APPENDIX 4:

VISCOSITY TEST

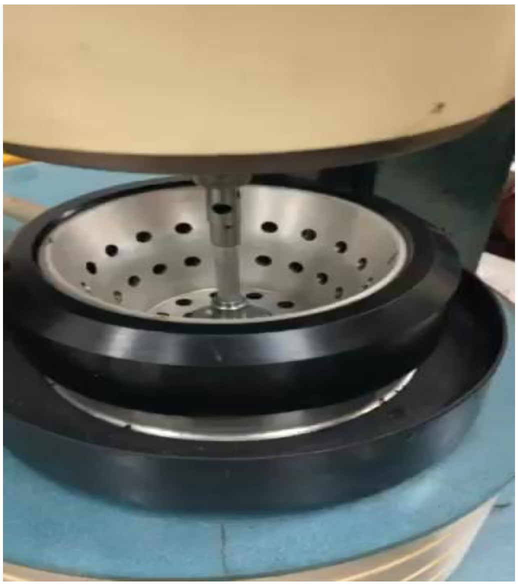
Tube sample for viscosity

Tube sample for viscosity

APPENDIX 5:

DYNAMIC SHEAR RHEOMETER

Dynamic shear rheometer



Dynamic shear rheometer

Sample of dynamic shear rheometer test

Equipment for taking sample of dynamic shear rheometer test