ROLE OF REJUVENATORS AND THEIR EFFECT ON THE PERFORMANCE AND AGING CHARACTERISTICS OF BITUMEN

PROJECT REPORT

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DECLARATION

I undersigned hereby declare that the project report "**Role of Rejuvenators and their Effect on the Performance and Aging Characteristics of Bitumen**", submitted for the partial fulfillment of the requirements for the award of the degree of Master of Technology of the APJ Abdul Kalam technological University, Kerala is a bonafide work done by me under the supervision of Dr. Kavitha Madhu, Associate Professor. This submission represents my idea in my own words and where the idea or words of others have been included, I have adequately and accurately cited and referenced the original sources. I also declare that I have adhered to ethics of academic honesty and integrity and have not misinterpreted or fabricated any data or fact or idea in my submission. I understand that any violation of the above will be a cause for disciplinary action by the institute and/or the University and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been obtained. This report has not been previously formed the basis for the award of any degree, diploma or similar title of any other university.

Kollam
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CERTIFICATE

Certified that this report entitled **“ROLE OF REJUVENATORS AND THEIR EFFECT ON THE PERFORMANCE AND AGING CHARACTERISTICS OF BITUMEN”** is the report of the project presented by **SUKANYA K. R., Reg. No.: TKM21CETE18** during **2022-2023** in partial fulfillment of the requirements for the award of the Degree of Master of Technology in Transportation Engineering of the A P J Abdul Kalam Technological University.

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ABSTRACT

The field of pavement engineering is at the verge of resource depletion and the need of construction materials are increasing in exponential manner, it is required to check the suitability of different alternative to replace the need of virgin materials. Suitability refers to the structural and functional performance of the pavement towards loading and other external factors like solar radiation, environmental and climatic factors. In order to reduce the usage of non-renewable virgin raw materials for the construction of flexible pavement, milled material called Recycled Asphalt Pavement (RAP) can be used. Therefore, the work analyses the effect of rejuvenators in restoring the binder properties in a hot mix for pavement construction with RAP. Various tests based on physical, chemical and rheological properties were done to ascertain the suitability of binder. Rate of deterioration of binder properties due to various aging conditions like short term (Rolling Thin Film Oven -RTFO test) and long term (recovered RAP binder) aging are considered. Hence, rejuvenators which can be considered as modifiers of aged binder can be blended with RAP during hot mixing to restore the binder properties. Rejuvenators such as waste engine oil (WEO) and waste cooking oil (WCO) are adopted in the study to check the structural and functional contribution of reusing binder. Chemical analysis includes Fourier Transform Infrared Spectroscopy (FTIR) to find the aging indices and rheological analysis includes dynamic Shear Rheometer to compare the complex shear modulus (G*) and phase angle (δ) for predicting fatigue and rutting behavior. Based on the test results WCO is found effective in restoring physical properties, in rheological properties RAP binder modified with rejuvenators are found comparable to VG 30.

***Keywords**: Recycled Asphalt Pavement, Rejuvenators, RTFO, FTIR, DSR, Complex Shear Modulus, Phase Angle*

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ABBREVIATIONS

AASHTO	American Association of State Highway Transportation Officials
ASTM	American Society for Testing and Materials
IS	Indian Standards
IRC	Indian Road Congress
VG	Viscosity Grade

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Road infrastructure is an index of development among nations. Indian Government itself is providing utmost priority to highway development, hence introduced ‘Bharathmala ‘project. This is a central government initiative under which the road network constructions are implementing. These initiatives made India, the country having second largest road network in the world with a stretch of 63.75 lakh km, as per Ministry of Road Transport and Highways. Major portion of road stretch constitute flexible type and bitumen being the component which provides flexibility to the pavement; there by binder property, availability and material cost are significant. Bitumen being the by-product of distillation of crude oil, the cost of crude oil in the world market will affect the cost and availability of the binder (Attanasi, 2008). Not even bitumen, aggregate fraction also being non-renewable, is facing depletion due to exponential increase in the construction activities and will continue to an extended period if no measures are taken to optimize the utilization. One among such measures is adopting the principle of 3R’s: reduce, recycle and reuse or else opt for alternative materials for the partial or complete replacement of non- renewable natural resources as step towards sustainable development (Plati, 2019). This study focusses on reducing the usage of virgin materials; recycling and reusing aged materials. Flexible pavement constitutes non-renewable raw materials from the subgrade to surface course and when there is need for maintenance, rehabilitation or even the construction of new pavement, designers can opt for existing pavement materials. Studies have proven that milled materials from flexible pavements have a scope of reuse and this concept of recycling is defined as Recycled Asphalt Pavements (RAP).

RAP is a reusable aged material obtained from flexible pavement where the aging happened due to various agents like environment, climate and traffic. Severity in such conditions will define the degree of aging. Hence, the various aging conditions prevailing are ultra violet aging, air, solar light, water with different pH, salinity, coastal vicinity and so on. Such factors can primarily affect the binder property than the aggregate fraction since binder acts as an impermeable coating to the aggregates. This can affect various properties of binder such as morphology, physical, chemical and rheology; in-turn negatively affects the structural and functional performance of pavement, its durability and life of the pavement. Therefore, degree of aging of binder needs considerable attention and adoption of measures to reduce the aging effect can contribute various advantages to the field of pavement engineering. Adoption of rejuvenator is an effective way to reduce the aging effect, whether for reusing the aged RAP or to make minor repair and maintenance works. Here is the importance of studying different aging conditions, degree of aging in bitumen and role of rejuvenators to restore the aged properties.

1.2 AGING IN BITUMEN

Aging can be defined as any sort of deterioration in properties of bitumen due to various reasons. During construction of pavement there is possibility of short-term aging which is happening at comparatively higher rate due high temperature application during the mixing, laying and compaction of bituminous concrete. This is followed by long term aging during the in-service life of a pavement along which the pavement is subjected to various environmental, climatic factors and repeated traffic loading. RAP is the aged flexible pavement residue with immense recycle-reuse value subjected to long term aging with some residual properties, hence is a sustainable practice of road construction with cost effectiveness. IRC 120-2015 contains the recommended practice for recycling of asphalt pavement. As per the code maximum proportion of RAP to be incorporated in a fresh mix of bituminous pavement is about 30% if in-plant recycling and about 100% if in-place recycling is adopted. The residual properties may not be sufficient or cannot make the material suitable for reuse unless we restore the properties. There are various materials which are bio and chemical in nature and can contribute to considerable extent in restoring the bitumen properties under morphological, physical, chemical and rheological categories. These materials are defined as rejuvenators.

1.3 REJUVENATORS

Rejuvenators are additives or modifiers that can improve the eroded properties of aged bitumen, especially engineering and rheological properties of binder by restoring their micro structure (Cavalli et al., 2018). They may be commercially available chemical materials, or any bio based or fossil-based oil medium that can rejuvenate the aged binder properties. Studies have introduced certain materials like waste engine oil, waste cooking oil, soybean oil, castor oil and some commercial products as rejuvenators are added in different percentages of the bitumen content.

Even though rejuvenators are meant for enhancing the properties their presence can somewhere negatively influence certain properties like rutting resistance. To quantify the variation in properties of virgin bitumen and aged bitumen, there are different ways; either simulate different aging conditions like short term and long-term aging or consider the RAP binder, or else simulate aging due to various pH and saline conditions. The process of extraction and recovery of aged bitumen is the pre- requisite for conducting tests on the rejuvenated binder material from RAP.

1.4 OBJECTIVES OF STUDY

Based on the literatures and considering the importance in restoring the properties of binder due to aging, this study focuses on understanding different properties of binder with and without rejuvenators. This can help in developing an insight about aging mechanism, rejuvenation, changes in physical, chemical and rheological properties of bitumen under various aging and rejuvenation conditions. Therefore, the work is based on the following objectives:

1. To study the compatibility between virgin binder (VG 30) and rejuvenators (Waste Engine Oil and Waste Cooking Oil).
2. To compare the physical properties of unaged, aged bitumen with and without rejuvenators in different proportion and to arrive at an optimum dosage.
3. To conduct chemical analysis of unaged, aged bitumen with and without rejuvenators at optimum dosage.
4. To conduct rheological analysis of unaged, aged bitumen with and without rejuvenators at optimum dosage.

1.5 SUMMARY

Alternate pavement materials were already in use like plastic, polymer, crumb rubber, coir fibre which can also be defined as modifiers. Introduction of modifiers are always appreciable provided they must be compatible with the existing pavement materials. The question of compatibility can be neglected in case of RAP, but the effective recycling is possible only after rejuvenation. There are different categories of rejuvenators based on the availability, origin and its chemical properties. Reuse of RAP and addition of rejuvenators, especially bio-oil or residual fossil oil may be a choice of sustainable pavement construction.

Introduction chapter describes about the topic and its relevance in the current environmental condition. Chapter 2 includes literature review which helped to get an insight about the advancements in the field of pavement materials and scope of research in the respective field, from which the objectives were derived. Methodology is included in Chapter 3, which includes the experimental plans and the sequence of execution of each task for accomplishing the project work. Chapter 4 contains the test results and discussions based on the laboratory experiments. This section performs a detailed analysis of results to arrive at inferences which may be helpful in developing insights on binder aging, rejuvenation and pavement construction. Chapter 5 include conclusions made from the study and future scope of the work, which is followed by the reference chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

The field of pavement engineering are facing lack of construction materials. This situation initiates the reuse of existing materials and milled materials obtained from flexible pavement which are having greater reuse value. Before reusing there is a need for evaluating the properties of various components from the milled material since they have undergone various types of property deterioration. It requires thorough insight about various binder properties when flexible pavement materials are to be reused. Therefore, from literature review binder aging, factors influencing aging, influence of aging on various properties of binder, conventional and advanced techniques to quantify the degree of aging, methods to restore properties while reusing bituminous materials are certain aspects that are familiarised.

2.2 RECYCLED ASPHALT PAVEMENT

Recycled Asphalt Pavement (RAP) is obtained by milling the existing flexible pavement, when the pavement become in-serviceable due to many reasons. By the addition of rejuvenators, RAP can be recycled and reused as flexible pavement materials and is suitable for the construction of any layers of the pavement. Algin et al. (2022) says that RAP can be used as sub base material with and without cement stabilization. Strength of RAP is again assured in the studies conducted by Ullah and Tanyu (2019) and Seferoglu (2018). They have experimented RAP as base material and found out that this material can be adopted as unbound base material also. Reuse of RAP primarily concentrates on the binder property where there is immense scope of research on aging mechanisms, restoration of properties with different modifiers and so on.

2.2.1 Bitumen and Ageing Mechanism

Bitumen can be defined as hydrocarbon obtained by removing lighter fractions like petroleum gas, petrol and diesel from crude oil during the refining process. Tauste et al. (2018) studied the composition of bitumen and defines that there are two major components of bitumen like asphaltene (5- 25%) and maltenes, maltenes further constitutes saturates (1-25%), aromatics (40-60%) and resins (5-50%). In the same study the author differentiates the stages of ageing as short term ageing and long-term ageing. Short term ageing is defined as the property deterioration during hot mixing, its transportation, laying and compaction while long term ageing is during its service life. Based on the factor influencing ageing, there are different mechanisms of ageing like oxidation, evaporation, steric hardening and the rate of ageing can be enhanced by UV radiations. The author defines oxidation as the removal of hydrogen from the hydrocarbon by oxygen, resulting in the variation in composition of asphaltene, resin and aromatics. This finally results in the formation of sulfoxides and carbonyl compounds which are the indicators of oxidation. Oxidation can disturb the colloidal state of bitumen. Evaporation is an irreversible process in which volatile compounds (saturates and aromatics) are lost during heating (mixing and laying). This phenomenon depends mainly on temperature and other exposure conditions. Third process of steric hardening is a reversible process that changes the rheological properties of bitumen without altering its chemical composition.

2.3 EXTRACTION AND RECOVERY OF BITUMEN

2.3.1 Methods of Extraction

Extraction is the method of separating bitumen from the aggregate surface by adding certain solvents aided with mechanical devices. There are cold and hot methods of extraction which can further influence the properties of extracted binder. Different methods, their working conditions, advantages and limitations obtained from the study of Mikhailenko et al. (2019) are tabulated as Table 2.1. Table states that there are five different methods of solvent extraction and centrifugal extraction is the most commonly adopted method because of lesser negative impacts and the possibility of later recovery of binder.

2.3.2 Methods of Recovery

Methods of extraction is followed by recovery methods; to separate solvents from binder. Abson method and rotary evaporator are the two different methods conducted under hot conditions. Tests results of such recovered binder says that there is no significant effect of higher temperature on the binder properties during extraction. Table 2.2 and Table 2.3 shows binder recovery methods and their features, solvents adopted as per Mikhailenko et al. (2019). Some of the solvents possess health and environment hazards therefore immense care need to be taken while handling with these materials, personal protection equipment is recommended to use under such situations**.** The Table

2.2 includes the features of commonly adopted recovery methods. Table 2.3 includes solvent used for the extraction and they shall be completely removed from the binder-solvent solution so that the recovered binder shall contain only the binder without any external components.

Table 2.1: Different Methods of Binder Extraction (Mikhailenko et al., 2019)

Methods	Temperature Condition	Features/ Advantages	Limitations
Centrifuge	Room temperature or cold method	Most common, less ageing, safer to operate, preferred to reflux method, later recovery is possible	Not as effective in removing binder from aggregate and crumb rubber modified binder
Reflux	Temperature higher than room temperature	Common method, more effective in dissolving binder than centrifuge, more accurate result for binder content	Heating cause ageing and risk to users
Vacuum	Room temperature	Most accurate result for binder content when mixture has highly variable and absorptive aggregates	Difficult to clean, less in use
SHRP	Room temperature	Modified centrifuge extraction combined with Rotovap recovery, less ageing than reflux method	Expensive, labour intensive, time consuming
Automatic	Varies	Reduce labour time, less exposure to toxic chemicals, require less operation skill, consistent than reflux method	Expensive design

Table 2.2: Different Methods of Recovery of Binder (Mikhailenko et al., 2019)

Methods of recovery	Features
Abson Recovery	• Hot condition (chances of hardening) • Widely used • Inexpensive
Rotary Evaporation/ Rotovap	• Hot condition (chances of hardening) • Relatively less binder ageing and residual solvent compared to Abson • Less labour

Table 2.3: Solvents for Extraction (Mikhailenko et al., 2019)

Solvents	Advantages	Limitations
Carbon di sulphide	Low cost	Flammable and health concerns
Trichloro ethane	Widely used, evaporates quickly, reusable	Harmful for users and environment
Toluene	Better for PMAs, relatively safe for user	Fire hazard
N- propyl bromide	Good with RAP, evaporates quickly, re-usable	Harmful for users and environment, health concerns, corrosive
Bio-Sourced (Limonene)	Green material	Expensive, high boiling point, high quantity required

Table shown above briefly explains the features, limitations and risks associated with different solvents available. This states the need for having personnel protection to the one who is handling the chemicals.

2.4 REJUVENATORS

Various studies have done in pavement engineering sector and the studies in general defines rejuvenators as additives which can reinstate the original physical and rheological properties of bitumen**.** Loise et al. (2019) says that rejuvenators can reduce the stiffness, viscosity and increase ductility and differentiated rejuvenators in to rheological and real rejuvenators. Xu et al. (2022) studied with industrial rejuvenators for introducing polarity to asphaltene rich domain. Banerji et al. (2022) considered waste engine oil and waste cooking oil as rejuvenators considering their behaviour as fluxing agent, where fluxing agents are rheological rejuvenators or softening agents. Studies also says that fatty acids can impart rejuvenation to binders. There are two requirements needed to be fulfilled by rejuvenators like high percentage of aromatics to disperse asphaltene and low percentage of saturates to be compatible with asphaltene. The dispersion rate of rejuvenators is governed by the viscosity of maltenes and rejuvenators usually furnish maltenes or oil fraction to binder to facilitate its uniform distribution. Xu et al. (2022) has introduced rejuvenation encapsulation technique which can be considered as a self-healing mechanism, in which calcium alginate capsules are embedded in the pavement. As the cracks appear and advances near the capsule, it gets burst out and rejuvenator is released to heal the crack. To quantify the effect of rejuvenation, researcher have to conduct certain lab tests on the aged binder and compare the same with virgin binder. There are various tests available based on the properties of bitumen. Table 2.4 enumerates various binder properties, corresponding tests and their objectives Zhang et at. (2022). Table 2.5 includes various rejuvenators come across during the review process.

Table 2.4: Binder Properties, Tests and Parameters Analysed (Zhang et al., 2022)

Property of Bitumen	Tests and Parameters Analysed
Morphological	Scanning electron microscope- indicate micro surface character Atomic force microscopy- evaluate the inner morphology of bitumen
Chemical	FTIR Spectrometer - Amount of carbonyl and sulfoxide groups formed by ageing or by various chemical reactions SARA analysis - To understand the chemical composition of bitumen Gel Penetration Chromatography (Huang et al., 2021) - To obtain molecular weight and molecular size distribution of sample
Physical	Softening Point Test - To determine the temperature susceptibility Penetration Test - To determine the hardness of bitumen Viscosity Test - To measure the consistency of bitumen
Rheological	Dynamic Shear Rheometer Temperature Sweep Test - Permanent deformation resistance of bitumen under moderate temperature range Multiple Shear Creep Recovery Test - To find permanent deformation and elastic recovery of bitumen Linear Amplitude Sweep Test - To characterize the fatigue resistance Beam Bending Rheometer - To investigate the low temperature rheological properties of bitumen under different conditions

Above table help to have an idea about various tests available to quantify the properties of binder under various environmental and traffic conditions.

Table 2.5: Enumerating Rejuvenators, Properties and Related Studies

Rejuvenators	Properties	Author
Industrial rejuvenator	To introduce polar functionalities in asphaltene rich domains	Xu et al., 2022
Waste engine oil/ cooking oil	Act as fluxing agent	Banerji et al., 2022
Polanga oil and reseed oil	Contain fatty acid like oleic acid and linoleic acid which helps to reinstate properties	Pradhan et al.,2020 Xu et al., 2022

The above table describes certain rejuvenators and their properties because of which the author has chosen the material for rejuvenation mechanism. Fatty acids containing oleic acid and linoleic acids are found to be effective in restoring properties by enriching the maltene phase.

2.5 EFFECT OF REJUVENATION ON VARIOUS PROPERTIES OF BINDER

Behnood (2019) and Zhou et al. (2018) conducted study about different categories of bio-oil as rejuvenators and how they take part in rejuvenation. Three types of bio-oil are from agricultural products, wood waste and plant oil; animal waste; waste oil like waste cooking oil. Zhou et al. (2018) states that total fatty acids present in bio-oils can be considered as an indicator of effectiveness of bio- rejuvenators and saturated fatty acids as the indicator of adverse effects of wax in the binder. Zaumanis et al. (2015) concludes that organic or vegetable oils are much efficient in restoring the binder properties in lesser dosage than petroleum-based engine oil. Tabatabaee and Kurth (2017) also categorised rejuvenators as three; soluble softeners which are highly compatible with naphthenic aromatic components of bitumen, compatibilizers which have affinity towards all the fractions of bitumen and insoluble softeners.

2.5.1 Rejuvenation on Physical Property

Banerji et al. (2022) states that rejuvenators have different degree of rejuvenation on same grade of bitumen. For unmodified binders, if waste cooking oil is having higher degree of rejuvenation, then waste engine oil is having better performance in case of modified bitumen. Kuang et al. (2019) conducted physical property analysis on binder in different degree of aging and rejuvenators are found to be effective. Rejuvenators contains lesser content of asphaltenes and oil with higher content of saturates and aromatics. Zhang et al. (2021) studied the physical properties of RAP and role of self- developed rejuvenators. Study concluded that the rejuvenator is able to achieve the technical requirements of control mix; rejuvenator in this study is a mixture of aromatic oil, plasticizers and anti-stripping agents.

2.5.2 Rejuvenation on Chemical Property

Studies revealed that there are various chemical reactions taking place in a binder due to aging and the nature of reaction or the products formed may be based on the factor responsible for aging.

Major reason behind binder aging is oxidation due to which sulfoxides and carbonyl compounds were formed which represents short term and long-term aging respectively. Other than oxidation there are chances of aromatization, changes in aliphatic compounds and long chains. At the same time there are relative variations in the asphaltenes and maltenes (maltenes constitutes saturates, aromatics and resins) in relation with aging.

From the review process it can be stated that there are different techniques available for conducting the chemical analysis of binder property. Some of the major techniques are Fourier Transform Infrared Spectroscopy, UV vis spectrometer, SARA analysis, CHNS analysis, Gel Penetration Chromatography and so on. Among them FTIR is considered to be efficient in quantifying the aging in modified and unmodified bitumen. These methods are useful in quantifying various aspects of unaged, aged, modified and rejuvenated asphalt binder.

2.5.2.1 FTIR

Marsac et al. (2014) defines chemical analysis using FTIR such that, there is definite pattern of vibration or interaction between chemical components and IR radiations. This depends on the type of bonds present and the band width that interact with the chemical bond. Each bond reacts with only a specific IR band and is considered as the finger print of that particular chemical compound. FTIR measurement principle may be based on absorbance or reflectance. In Attenuated Total Reflectance (ATR), there is a crystal with high refractive index which is in contact with the sample. IR beam enters the crystal and after one or two reflections, the attenuated wave properties are studied. Nivitha et al. (2016) conducted a study on binder, its aging and role of additives exclusively using FTIR. The study analysed characteristic peaks and indices like carbonyls, sulfoxides, aliphatic, aromatics and long chain and concluded that carbonyl and sulfoxide indices show a linear increase with aging. Author states there is a relative increase in aromatic fraction during the initial stages of aging and aliphatic fraction reduces as the aromatic fraction shows an increase. Another study conducted by Hofko et al. (2018) considered the variations in chemical properties of RTFO aged binder at different temperature and PAV aged binder using FTIR test for verifying the reproducibility. Findings from the study says that there is an increase in the sulfoxide index with increase in temperature. This could help in making the inference that there is significant impact of mixing temperature on sulfoxide index than carbonyls. Carbonyl index shows considerable variation or long-term aging effect among unaged, RTFO aged and PAV aged binder.

2.5.2.2 Saturates Aromatics Resins Asphaltenes (SARA) Analysis

Al-saffar et al. (2021) performed the separation of maltenes into resins, aromatics and saturates as per ASTM 4124. From the maltene phase, saturates were separated using 50ml n-heptane. Then 100 ml of toluene followed by 75 ml blend of methanol and toluene (50:50) was used to separate aromatics.150 ml of trichloroethylene was used to separate resins. Author says that the saturate fraction eluate was colourless, naphthenes aromatics was yellow and resins are black in colour. Ren et al. (2021) conducted Thin Layer Chromatography with Flame Ionization Detection (TLC-FID) to quantify the SARA compounds in aged and unaged binder. This is aided with hydrogen and air flow at a rate of 160 ml/minute and 2 l/min respectively. Bitumen sample of 0.1 gm was dissolved in 10 ml of toluene was subjected to chromatography separation with silica chrome rod. After conducting chromatographic separation, n-heptane is used to separate the saturates, at the same time aromatic and resin fraction can be separated in toluene/n-heptane (80:20), dichloromethane/ methanol (95:5) respectively.

2.5.2.3 Carbon Hydrogen Nitrogen Sulphur (CHNS) Analysis

Nivitha et al. (2016) conducted the elemental analysis where samples were contained in Tin boats and Tungsten catalyst. Oxides of C, H, N, S were formed by heating the sample at 1000°C. Specific absorption columns were used to identify these oxides and thermal conductivity detectors are used to identify each element.

2.5.2.4 Atomic Force Microscopy (AFM)

Prosperi and Bocci (2021) conducted a non- destructive analysis for analysing the morphology, stiffness, cohesion and molecular interaction at microscopic level using AFM technique. This technique helps in identifying three phases in binder; catana phase/ bee phase which are hills found in the undulated AFM image, peri phase which surrounds the bee phase with roughness, para phase which is found next to peri phase and usually flat in pattern.

2.5.3 Rejuvenation on Rheological Property

The rheological characterisation for all asphalt binder samples was assessed by dynamic shear rheometer and beam bending rheometer. Rheological property includes the visco elastic nature of binder, its fatigue and rutting behaviour, response to temperature changes, elastic recovery etc.

2.5.3.1 Dynamic Shear Rheometer (DSR)

Zhang et al. (2020) has studied high, low and intermediate temperature performance of bitumen which is short term aged and the influence of bio-oil rejuvenators and crumb rubber modifier. Author has found the rutting and fatigue parameters using DSR and concluded that bio-oil like waste cooking oil can better restore the properties than fossil oil-based rejuvenators. Study of Zhang et al. (2020) analysed the rheological response of binder subjected to various rejuvenation. Strain sweep followed by frequency sweep test were conducted to check the viscoelastic nature of binder. Tests results showed the binder to be in linearly viscoelastic nature and to quantify complex shear modulus (G*) and phase angle (δ) frequency sweep test at three temperatures were done. Interpretation of master curves showed that highly aged binder possesses comparatively higher G* value and lower δ value; certain master curves nearly overlapped with that of the virgin bitumen. Hence concluded that aging effect made the bitumen stiffer and more elastic and waste engine oil rejuvenator is found to create some difficulties because of its lubricating effect.

Pradhan and Sahoo (2019) compared RAP and recovered binder properties using Polanga oil as rejuvenator, where rheological property is analysed by different DSR tests. Authors conducted frequency sweep, amplitude sweep, temperature sweep, creep recovery and fatigue tests to study various rheological parameters of binder. Within the range of 0.01-100 Hz of frequency and at varying strain rate frequency sweep test was conducted; amplitude sweep was done at a strain rate of 0-100% with a frequency of 1.59 and 10 Hz; Temperature sweep with 5° increments was conducted at a constant frequency of 10 Hz in strain-controlled mode. Creep recovery as per ASTM D 7405-15 was performed to assess the elastic response of asphalt binder at different stress levels. Fatigue test at a temperature of 10°C and a frequency of 10 Hz is maintained to determine the fatigue resistance under cyclic loading with linear amplitude sweep (LAS) test. Authors concluded that 5% Polanga oil rejuvenated aged binder acquired better rutting and fatigue resistance, better than unaged virgin binder.

Rathore et al. (2022) in their study has explained in detail about temperature and frequency sweep, linear amplitude sweep test and multiple stress creep recovery test. In temperature and frequency sweep, bitumen was heated to 20°C and subjected to varying frequencies between 0.1 to 30 Hz. Afterwards the sample is subjected to temperature gradient of 10°C up to 80°C; at each temperature the material is subjected to frequency sweep. A 25mm diameter spindle with 1 mm gap geometry is preferred. Aging index and softening index were calculated as a measure of binder aging; aging index indicates the increase in stiffness compared to virgin binder and softening index indicates the reduction in stiffness of recycled bitumen. Fatigue behaviour of binder is determined using LAS test as per AASHTO TP 101. First stage of the test is done with 8 mm diameter spindle and 2mm gap at a temperature of 25°C under frequency sweep condition. Second stage constitutes variation in strain linearly from 0.1 to 30% over loading cycles of 3100, at a particular frequency for a total test time of 310 seconds. Fatigue life is calculated using viscoelastic continuum damage model.

Micaelo et al. (2015) defines fatigue failure as the point at which the material's complex modulus value falls to 50% of its initial value, with the corresponding number of cycles denoted as $N_{f,50}$. Another approach to quantify fatigue resistance of asphalt is termed as Dissipated Energy (DE), which is formed due to cyclic loading. Area under hysteresis loop is termed as DE density and is calculated using numerical integration. Guo et al. (2021) in their study says that complex modulus of modified binder increases with age. Among different types of rejuvenators like warm mix rejuvenators can reduce the complex modulus of virgin binder and differently modified binders; followed by commercial rejuvenators and aromatic oils. Commercial rejuvenators can better recover the modulus of long-term aged binder.

2.5.3.2 Beam Bending Rheometer (BBR)

BBR test evaluates the low temperature performance of binder. Huang et al. (2019) conducted the test to find the creep stiffness and m- value; where m-value is considered as an indicator of bitumen stiffness sensitivity with time and stress relaxation ability. The study found that creep stiffness increases and m-value decreases for all the samples with decrease in temperature. Author also concluded that higher stiffness corresponds to smaller creep compliance, then greater stress may be required to produce a unit strain on binder. Al-saffar et al. (2021) also tried to evaluate the low temperature behaviour of bitumen as per ASTM D 6648. Authors studied the response of an asphalt beam subjected to 100g loading weighing at different temperatures to compute the creep stiffness (S) and material relaxation constant (m-value).

2.5.4 Rejuvenation on Morphological Property

Morphology refers to the surface character of a material and Scanning Electron Microscopy can be performed to study micro level surface features of bitumen. Meng et al. (2022) conducted SEM on salt eroded bitumen; wrinkles, pits, cracks, roughness and salt crystal in needle, rods, crystals were identified. Mazumder et al. (2018) introduces SEM as a versatile tool that allows the researcher to observe and evaluate heterogenous organic and inorganic materials in micro to nanometre scale; even 3-D imaging is possible with the technique. Here the specimen surface is subjected to finely focussed electron beam, after interacting with the surface different types of signals come out like secondary electron, back scatter electron, characteristic X-ray and other photons of different energy. These signals are detected with suitable detectors and analysed to characterise the sample, say crystalline, topography and composition.

From the review process certain gaps identified are such that a thorough comparison between degree of aging between RTFO aged and RAP binder with respect to unaged VG 30 is needed. It was required to have a comparison between the optimum dosage of rejuvenators (WEO and WCO) on RTFO aged binder and RAP binder, identification of presence of similar functional groups in binder samples and rejuvenators. Another gap identified was to check whether the optimum dosage of both the rejuvenators satisfies various property restoration after rejuvenation.

2.6 SUMMARY

In general, this review process revealed the scope of RAP as pavement material and the role of rejuvenators in enhancing the binder properties. Also, studies concluded that RAP have sufficient strength to serve as a pavement material within the proportion, 30- 40% in hot mix. Among different types of rejuvenators, there are real and rheological rejuvenators; bio-oil based and fossil oil based; chemical rejuvenators. Any of such types can enhance the binder properties but beyond certain dosage, it may negatively affect the functional and structural behaviour of pavement. Present study finds the optimum dosage of rejuvenators and variations in physical, chemical and rheological properties of aged binder due to rejuvenation.

CHAPTER 3

METHODOLOGY

3.1 GENERAL

This work is based on the comparison between unaged and aged bitumen and its scope of reuse by the addition of rejuvenators. Aging simulated binder and RAP binder were adopted. From the RAP, binder is extracted and recovered by standard recommended methods. To have an insight about different degree of aging, a comparative study is proposed between virgin binder, short term aged binder and long-term aged binder recovered from the RAP materials. Physical, chemical and rheological analysis of the above-mentioned binder category is studied with and without the rejuvenators, to check its suitability to reuse.

3.2 DETAILED METHODOLOGY

Methodology includes the experimental plan developed to accomplish the project in terms of collection of sample materials, various laboratory experiments and order of execution of tests. A detailed methodology can very well facilitate the time bound and efficient completion of the project. Thorough literature review is found to be helpful in developing a work plan and familiarizing various techniques evolved in the field of pavement engineering. Figure 3.1 is the diagrammatic representation of methodology adopted for this particular study.

Step 1: To check the compatibility between rejuvenators and bitumen, specific gravity test using pycnometer (IS 1203), determination of flash point using Cleavland open cup apparatus (IS 1448 P-69) were done on VG 30, waste engine oil (fossil oil) and waste cooking oil (bio-oil).

Step 2: To compare the degree of aging between virgin VG 30 with short term and long-term aged VG 30, different aging conditions like rolling thin film oven test as per ASTM D 2872 for simulating short term aging and long-term aging with the binder recovered from RAP are used. Centrifugal extraction (ASTM D 2172) with trichloroethylene as the solvent followed by Abson recovery of extracted binder (ASTM D 1856) are performed.

Step 3: To check the various categorical properties of unaged and aged binder.

Step 3a: To check the suitability of reusing aged bitumen, to check the role of rejuvenators on binder properties based on physical, chemical and rheological behavior and to compared at different dosages of rejuvenators.

Step 3b: To determine the optimum dosage of both rejuvenators from RTFO aged bitumen and recovered RAP binder.

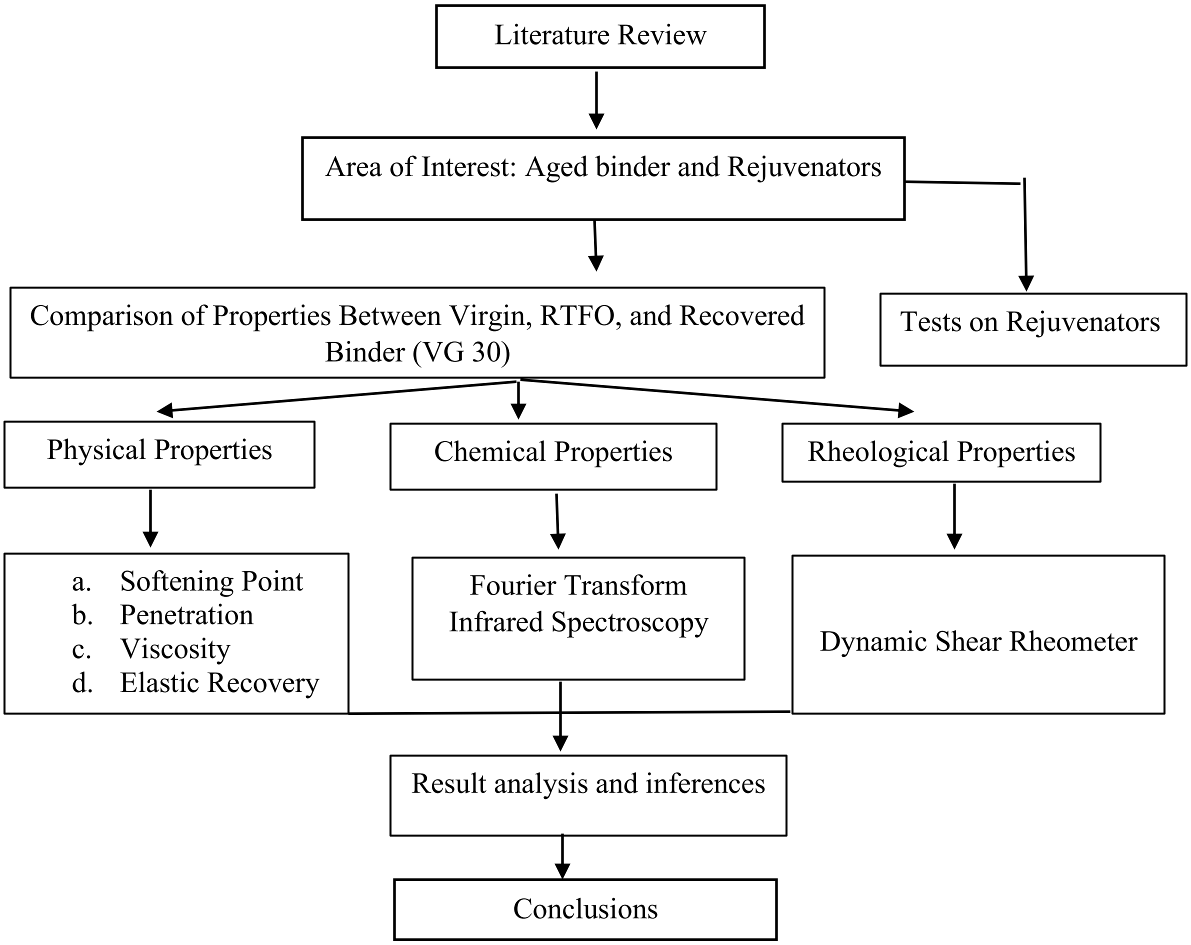

Figure 3.1: Flow Chart Showing Methodology

3.3 MATERIALS USED

3.3.1 Virgin Binder

This work has been done with viscosity grade (VG) 30 bitumen. As per IRC 111- 2009 (Specification for Dense Graded Bituminous Mixtures) Table 2, VG 30 is adopted in almost all the pavement works in India in lieu of old 60/70 penetration. Various physical properties like elastic recovery (ASTM D 6084), softening point (IS 1205), penetration (IS 1203), viscosity (ASTM D

4402) tests need to be done and verified as per IS 73- 2013. The same need to be done with RTFO aged and recovered binder; with and without rejuvenators.

3.3.2 Rolling Thin Film Oven (RTFO) Aging (ASTM D 2872)

This aging simulation is adopted for inducing short term aging in the binder which is supposed to be happened during hot mixing, laying and compaction of bituminous concrete at the field. This is under high temperature and major fraction of aging happened in this phase. Regarding the conditioning of bitumen as per code, following procedure is adopted. Figure 3.2 and Figure 3.3 represents RTFO aging equipment and the aging chamber respectively.

i. Heat the binder in the oven at a temperature of 150°C up to minimum time at which the binder turns to liquid state.
ii. Pour 35±0.5 gm of bitumen in to required number of glass containers.
iii. Immediately after pouring the sample, keep the container in horizontal position without rotating or twisting on a cooling rack, away from any source of heat.
iv. Allow the container to cool up to a minimum duration of 60 minutes and maximum of 180 minutes.
v. With the oven at operating temperature, 163°C and air flow set at 4000± 200 ml/min arrange the containers holding the sample in the carriage assembly.
vi. Fill any unused space with empty containers, close the door and rotate the assembly at a rate of 15±0.2 r/min. and maintain it for 83 minutes.
vii. At the conclusion of testing period, remove any sample for mass change determination and place them horizontally on a cooling rack.
viii. The final container shall be removed from the assembly within 5 min of removal of the initial container.
ix. After removing the residue from each of the glass containers, gently stir the collection container to homogenies the residue without entering air in it.
x. Always use a collection container with a volume of thirty times than the volume of RTFO aged residue.
xi. Test the residue within 72 hours of performing the RTFO aging.

3.3.3 RAP Binder, Extraction and Recovery

RAP is collected from NH stretch from Karunagappally to Chakkuvalli route, which was aged to 9 years. Binder from the RAP is extracted with the solvent trichloro ethylene using centrifugal extraction method as per ASTM D 2172, followed by recovery of binder from the extracted solution using Abson method (ASTM D 1856).

Figure 3.2 : RTFO Aging Equipment

Figure 3.3 : Aging Chamber

3.3.3.1 Extraction of binder

One of the common solvent extraction method, centrifugal extraction as per ASTM D 2172 is conducted to separate the RAP binder from the milled RAP material. Stipulated quantity, around 650-2500 grams of RAP fragments were taken in extractor bowl and immerse it with trichloroethylene or n-propyl bromide or methylene chloride (200 ml) and cover it with a filter paper and ring. Bowl may be rotated up to a speed of 3600 r/min, manually or mechanically and the extracted RAP binder can be collected from the outlet. Figure 3.4 and Figure 3.5 represents the centrifugal extraction of binder and the bowl with extracted binder respectively.

3.3.3.2 Recovery of binder

Abson recovery as per ASTM D 1856 is conducted to separate binder from the solvent used for extraction. Extracted binder is subjected to primary distillation so that major fraction of solvent, trichloroethylene can be separated from the RAP – solvent solution. Residue after primary distillation is then subjected to Abson method of recovery. Here the sample is subjected to heating at a stipulated rate. When the temperature reaches 135°C, provide CO_2 supply at a rate of 100ml/minute. When temperature rises to or above 160°C rate of supply shall be maintained at 900 ml/minute. This will help in removing the left-over solvent after primary distillation process. Figure 3.6 and Figure 3.7 represents primary distillation unit and Abson recovery apparatus for executing binder recovery.

Figure 3.4: Centrifugal Extractor

Figure 3.5: Bowl with Extracted Binder

Figure 3.6: Primary Distillation Unit

Figure 3.7: Abson Recovery Apparatus

3.3.4 Rejuvenators

Rejuvenators are additives or fluxing or softening agents added to aged binders so that the deteriorated properties of binder can be restored. There are different types of rejuvenators familiarized from literatures, among them this study considers waste engine oil and waste cooking oil as they are readily available in Kerala and is shown in Figure 3.8 Among the two types of rejuvenators considered in the study, one is fossil oil based (waste engine oil) and the other is bio-oil based (waste cooking oil).

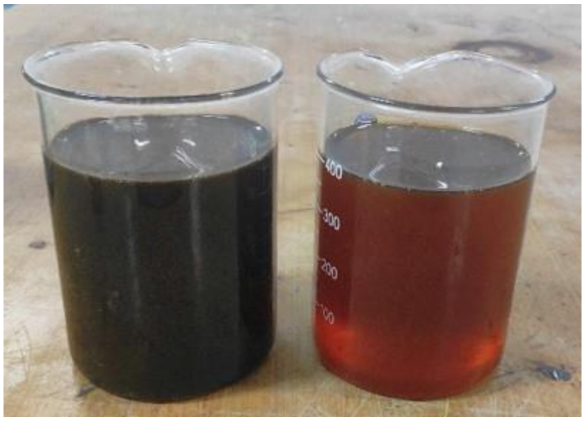

Figure 3.8: WEO and WCO

(Source: Banerji et al., 2022)

3.4 TESTS CONDUCTED

The materials considered in the study are subjected to various tests to quantify its physical and chemical properties, with and without rejuvenators. Under physical property, softening point test using ring and ball apparatus, penetration test using penetrometer, dynamic viscosity test by brookfield viscometer, elastic recovery using briquette mould with certain modifications are used. These tests are repeated with and without the rejuvenators at different dosages, so that an optimum dosage can be determined. The same binder types are then subjected to chemical analysis using FTIR test, so that the characteristic functional group and aging indices can be found out. Another most important property of the binder is its rheological property or the visco- elastic property which can be tested using a dynamic shear rheometer. Using the apparatus complex shear modulus and phase angle can be determined to verify the rutting and fatigue criteria.

3.4.1 Physical Property Tests on Binder

3.4.1.1 Softening Point Test (IS 1205- 1978)

Heat the bitumen to a temperature of 70 to 100 degree Celsius. Pour it in to the ring. Prior to pouring bottom surface of the base plate must be applied with equal amount of glycerine and dextrin to avoid sticking. Provide an air cool for the specimen for 30 minutes and place the ring in the ring and ball assembly, immerse in water. Keep a thermometer in the arrangement to read the temperature. As the temperature increase the bitumen gets soften and the ball start penetrating. Note the temperature at which the ball touches the bottom of the assembly and end point is as shown in Figure 3.9. Softening point will be expressed as the average of temperature for both the balls touching the bottom.

3.4.1.2 Penetration Test

Heat the bitumen to a temperature of 70 to 100 degree Celsius. Pour it in to the container up to 10mm below the top. Allow the binder to cool down to 25-degree Celsius temperature. Place the bitumen specimen under the penetrometer and allow the 25gm weigh needle to penetrate the bitumen for 5 seconds. Depth penetrated by the needle within the specified time is expressed as penetration value and the experimental set up is as shown in Figure 3.10.

Figure 3.9: Determination of Softening Point

Figure 3.10: Determination of Penetration Value

3.4.1.3 Elastic Recovery Test (ASTM D 6084)

This method is used to measure the elastic recovery of asphaltic material, by measuring the recoverable strain after severing an elongated briquette specimen of the sample as shown in figure 10. Assemble the mould on a brass plate and apply release agent on the surface of plate and the interior of the mould. Heat the sample to required temperature, stir it well and pour it into the mould. Allow it to cool at room temperature for 35±5 minutes followed by a water bath of another 30±5 minutes. Then trim the excess binder using a hot knife and make it level with the mould. Place the assembly in a water bath for 90 ± 5 minutes prior to testing, remove the side plates and fix it in the testing apparatus. Testing temperature shall be of 25°C, and speed of testing is 5cm/minute ± 5 %. Elongate the sample up to 10 cm and cut the specimen at its centre; leave it at that state for 1 hour. After the specified time, make the severed ends of the specimen to touch and measure the length of recovery from the scale. Figure 3.11 shows sample subjected to elastic recovery test. Express the recovery in percentage as per Equation 3.1 to compare the elastic property of binder. As per ASTM D 6084, percent recovery is expressed as,

$$\text{Recovery } \% = \frac{E-X}{E} * 100 \tag{3.1}$$

where,

E: original elongation of specimen, cm

X: elongation of the specimen, at the completion of the specified recovery time, with severed ends just touching, cm

3.4.1.4 Viscosity Test (ASTM D 4402)

This test is used to measure the apparent viscosity of asphalts at handling, mixing or application temperatures. In this specification, a rotational viscometer is used to measure the apparent viscosity of asphalt at elevated temperature. The torque on the apparatus- measuring geometry, rotating in a thermostatically conditioned sample holder containing a sample of asphalt, is used to measure the relative resistance to rotation. Take an approximate 8gm of binder in the container and condition it at a temperature between 75 to 100°C. Keep the container with binder in the thermocel. Before placing the container set the required temperature inside the thermocel, in this study apparent viscosity at 135°C is found out from the Brookfield viscometer. Spindle number 21 is the geometry chosen and the spindle rotating speed is fixed to be 20 rpm while conducting the experiment as shown in Figure 3.12. This experiment provides the dynamic viscosity in centi poise.

3.4.2 Chemical Property Test on Bitumen

Studies have proven that there are possibilities of molecular change during different stages of aging on the pavement binder along its service life. Different aging phenomenon are oxidation, evaporation, and steric hardening. Some of the advanced and commonly adopted techniques for chemical analysis are Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy, Thermo- Gravimetric Analysis (TGA), UV visible NIR spectroscopy, Carbon Hydrogen Nitrogen Sulphur (CHNS) analysis, Saturates Aromatics Resins Asphaltenes (SARA) analysis. Current work performs FTIR spectroscopy for analysing the degree of aging in terms of various indices and functional groups present in binder specimens and rejuvenators.

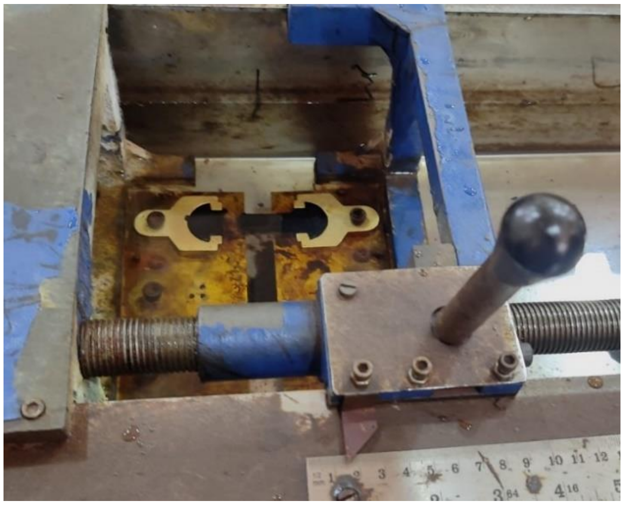

Figure 3.11: Elastic Recovery Test

Figure 3.12: Viscosity Test

3.4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

This is a chemical analysis technique in which the variations in chemical composition due to aging in bitumen can be interpreted using the FTIR spectra obtained from FTIR spectroscopy. This particular method makes use of infrared radiations within the electromagnetic spectrum to quantify the chemical changes taking place in a material by making use of the principle of Attenuated Total Reflectance (ATR). Controller software associated with the equipment will convert the attenuated properties of the IR radiations reflected from the material in to its Fourier transform. Peaks formed in the spectra is considered as the presence of functional groups, finger print compounds and newly formed compounds due to chemical changes as a result of aging in bitumen in the sample. Usually, indices corresponding to carbonyl, sulfoxides, aliphatic, aromatic and long chain compounds expressed in Equation 3.2, Equation 3.3, Equation 3.4, Equation 3.5 and Equation 3.6 are considered as the indicators of bitumen aging, with and without modifications. Figure 3.13 shows a particular model of FTIR Spectroscopy.

In this work, each bitumen sample (unaged VG 30, RTFO aged VG 30, RAP VG 30 and bitumen with rejuvenators) of 2gm weight is dissolved in 5 ml of trichloroethylene, taken in micro pipette is placed on the working platform of the equipment. Solvent gets evaporated and the bitumen residue is subjected to IR radiations after necessary adjustments including base correction. This work makes use of FTIR-ATR Schimadzu make with an associated controller software lab solutions IR. Number of scans applied is 45 and the resolution is 4 cm^{-1}. Wave number range considered for bitumen is between 4000 to 400 cm^{-1} and the spectrum is plotted in terms of % transmittance. Following are the formulas to calculate the indices like,

Carbonyl index (peak centred at wave number 1700) = $\mathbf{A}_{1678\text{-}1725}/\sum A$ (3.2)

Sulfoxide index (peak centred at 1030) = $A_{1010\text{-}1043}/\sum A$ (3.3)

Aliphatic index = $A_{1350\text{-}1510}/\sum A$ (3.4)

Aromatic index = $A_{1535\text{-}1625}/\sum A$ (3.5)

Long chain = $A_{715\text{-}733}/\sum A$ (3.6)

where,

$\mathbf{A}_{1678\text{-}1725}$: area of peak between wave numbers 1678 and 1725

$\mathbf{A}_{1010\text{-}1043}$: area of peak between wave numbers 1010 and 1043

$\mathbf{A}_{1535\text{-}1625}$: area of peak between wave numbers 1535 and 1625

$\mathbf{A}_{715\text{-}733}$: area of peak between wave numbers 715 and 733

A: Sum of areas $A_{1678\text{-}1725}$, $A_{1350\text{-}1510}$, $A_{1010\text{-}1043}$, $A_{715\text{-}733}$

Figure 3.13: FTIR Spectroscopy

3.4.3 Rheological Test on Bitumen

Rheology can be defined as the property of certain materials to flow in an unusual manner. In case of bituminous materials, property of rheology is very much important in analysing the rutting and bleeding of the binder that are in readily flowing conditions; and stiffness of bituminous mixture matters in terms of fatigue and cracking. Conventional tests like softening point, Elastic recovery using ductility testing apparatus, viscosity and flash point test can also be used to measure the rheology but with lesser reliability since the time dependant behaviour cannot be measured. Now-a-days rheology is usually measured with an oscillating equipment called Dynamic Shear Rheometer (DSR) introduced during Strategic Highway Research program. This equipment is well suited to quantify the viscous, elastic and visco elastic properties of bitumen.

3.4.3.1 Dynamic Shear Rheometer (DSR)

DSR is an advanced equipment which help in quantifying the visco-elastic / rheological properties of bitumen. In this project under DSR, Linear Amplitude Sweep Test (LAST) is conducted to find the complex shear modulus (G*) and phase angle (δ) to check the fatigue and rutting during the field performance. Both short-term and long-term aged bitumen is subjected to LAS test as per AASHTO T 101-14, 8 mm parallel plate geometry with 2mm gap is used for both rutting and fatigue parameter determination. The sample is subjected to shear under frequency sweep, oscillatory cyclic loading under linearly increasing amplitude at constant frequency, and under two temperature conditions in succession to find the rheological parameters. Figure 3.14 and Figure 3.15 represents the DSR and sample placed in DSR respectively.

Frequency Sweep Test (FST): FST is used under selected temperature and oscillatory shear loading at constant amplitude, variations in frequency are applied to study certain rheological property of bitumen at different ages. As per AASHTO T 101-14, 8mm parallel plate geometry with 2 mm gap is used. As per the DSR manufacturer's controller software, load is applied around 0.1 % strain over a frequency range from 0.2 to 30 Hz, to determine the complex shear modulus (G*) and phase angle (δ).

Linear Amplitude Sweep (LAS) Test: LAS test is conducted at required temperature using oscillatory shear and strain-controlled mode; at a constant frequency of 10 Hz. Continuous oscillatory strain sweeps with load increasing linearly from zero to 30% over the range of 3100 cycles of loading is applied. Shear strain and stress at the peak are recorded at every 10 load cycles (1 sec) along with the magnitude of phase angle, δ (degree) and complex shear modulus, G* (Pa).

Figure 3.14 : Dynamic Shear Rheometer

Figure 3.15: Sample Placed in DSR

3.5 SUMMARY

There are physical, chemical, rheological property tests to compare all the relevant properties of unaged, aged and rejuvenated binder so that the reusability or reproducibility of bitumen can be ascertained. Hence the project work includes softening point, penetration, viscosity and elastic recovery tests for physical property analysis. FTIR spectroscopy for chemical analysis and DSR for rheological analysis. The above-mentioned tests were done on samples with different dosages of rejuvenator so that the effect of rejuvenators can be compared and optimum dosage can be determined. Results obtained from the experiments are subjected to analysis and discussions to arrive at significant inferences, which will be demonstrated in the following chapter.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 INTRODUCTION

Aging in bitumen and the effectiveness of rejuvenators are quantified in terms of physical, chemical and rheological properties. Therefore, based on the objectives derived, laboratory works are classified in to different sub heads as follows:

- Conducting pycnometer test and flash point test for checking the compatibility between bitumen (VG 30) and rejuvenators - Waste Engine Oil (WEO) and Waste Cooking Oil (WCO).
- Conducting physical property tests on unaged and aged bitumen without and with rejuvenators in different proportion and to arrive at an optimum dosage.
- Conducting chemical analysis using Fourier Transform Infrared Spectroscopy on unaged and aged bitumen without and with rejuvenators at optimum dosage.
- Conducting rheological analysis on unaged and aged bitumen without and with rejuvenators at optimum dosage.

4.2 RESULT ON COMPATIBILITY BETWEEN VG 30 AND REJUVENATORS (WEO AND WCO)

This is to ensure compatibility between the binder and rejuvenators while hot mixing. It is verified by conducting specific gravity test using pycnometer bottle for binder and rejuvenators. Specific gravity values, if approximately same among the samples indicates better blending. Flash point test is conducted in terms of safety concerns by Cleveland open cup method as shown in Table 4.1

Table 4.1: Test Results on Checking Compatibility Between Binder and Rejuvenator

Tests	VG 30	WEO	WCO
Specific Gravity	1.02	0.874	0.92
Flash Point (Degree Celsius, ^{0}C)	220	237	>300

From the above test results certain inferences can be made which are crucial when two different materials are blended together. Specific gravity of pure bitumen is in the range of 0.97 to 1.02. Here, VG 30 sample satisfies the recommendation and specific gravity of WEO and WCO are around the specified range. This indicates better blending between bitumen and rejuvenators. As per IS 73, minimum flash point of any grade of bitumen is 220ºC and the bitumen sample satisfies the recommendation. Flash point of both the rejuvenators are well above 220ºC. This can avoid the possibility of catching fire when rejuvenators are blended with the binder while hot mixing. Since, both the criterion are satisfied compatibility check is assured.

4.3 COMPARISON BETWEEN PHYSICAL PROPERTY TESTS ON VG 30

This work concentrates on physical property tests like softening point, penetration, Brookfield viscosity and elastic recovery on VG 30 grade bitumen under different conditions like unaged, short term aged (RTFO) and in-service aged (RAP binder) without and with rejuvenators in different dosages. Comparison between different dosages of rejuvenators is intended to obtain the optimum dosage. Here test results obtained from samples of different degree of aging and rejuvenation are compared with unaged and non- rejuvenated VG 30, to arrive at an optimum rejuvenator dosage. On RTFO aged specimen, rejuvenators dosages adopted are 2,3 and 4 %; on RAP binder rejuvenator dosages are 3,4 and 5% respectively. Rejuvenator dosage for RAP has started with 3% since the optimum dosage for RTFO aging is 3% and assuming minimum rejuvenation on RAP can be attained only with this 3% rejuvenation. Table 4.2 enumerates the results of physical property tests on different specimens of binder with and without rejuvenators.

Comparing the test results, expected pattern of variation is obtained such that softening point, viscosity and elastic recovery are having continuous reduction and penetration of samples increased as the degree of aging increases. Hence can be concluded that, as the degree of aging increases serviceability of binder reduces due to the loss of various components in binder like SARA fractions, as a result of various factors influencing the binder properties like temperature, water at different pH and salinity, sunlight, other environmental factors, chemicals etc. This test results gave us an insight on the variation in hardness, temperature susceptibility, fluidity and elastic nature to recover the deformation due to loading and without the addition of any rejuvenators.

4.3.1 Variation in Physical Properties of Aged VG 30 without Rejuvenation

Comparison between variations in physical properties of aged VG 30 is done with RTFO aged and recovered binder samples subjected to various tests as shown in Table 4.2. The test results are compared with the recommendations in IS 73 and virgin VG 30, to check the effectiveness of rejuvenation.

Table 4.2: Variation in Physical Properties of Aged VG 30

Tests	As per IS 73	Virgin VG 30	RTFO Aged VG 30	Recovered VG 30 (from RAP)
Softening Point (ºC)	47 (min)	53.5	65	78
Penetration (0.1 Milli meter, mm)	45 (min)	45.2	24	8.3
Elastic Recovery (%) Recovery % = $\frac{E-X}{E} * 100$	-	15	4	Sample failed
Dynamic Viscosity (Centi Poise, cP) at 135ºC	350 (min)	453	673	748

There are certain inferences made from the test results to know the rate of change of properties due to different degree of aging. It is evident from the table that there is significant deterioration in binder properties when the sample is subjected to short term aging (RTFO aging) and for binder recovered from RAP which is 9 years old. Aging imparts hardness and brittle nature to binder with an increase in viscosity, lesser susceptibility to temperature and reduction in elastic recovery. Considering the softening point, there is an increase in softening point around 21.50% for RTFO aged sample and 45.80 % for RAP binder; 20% increase between RTFO and RAP binder. Aging can impart temperature resistance to the binder but while reusing, it become less susceptible to temperature making it less workable and reduce dispersion of rejuvenators. Considering penetration, decrease in penetration is about 46.5% for RTFO aged binder and 81.64% for RAP binder, which can be considered as an indicator of hardness in aged binder. Elastic recovery is considered as a measure of elastic nature of the binder, its ability to regain the original state after deformation. Elastic recovery reduced from VG 30 to RTFO aged binder and the test failed for

RAP binder since sample get extremely brittle due to long term aging. When variation in viscosity is studied, there is 48.57 % increase in viscosity for RTFO aged sample and 65.12 % for RAP binder; 11.14 % increase between RTFO and RAP binder. From the comparative studies based on laboratory experiments possible changes due to aging or reason behind variation in physical properties can be listed as oxidation, evaporation and steric hardening. Due to oxidation sulfur gets converted to sulfoxides and benzyl carbon in to carbonyl compounds. Respective changes can be explained in terms of relative variations in SARA fraction like flocculation of asphaltenes, increase in resins, consumption of aromatics and relative variation in saturates. All these changes can be quantified using chemical analysis techniques. Restoration in deteriorated binder properties due to aging can be done by rejuvenation and the effect of rejuvenation is studied here onwards.

4.3.2 Effect of WEO on Physical Properties of RTFO Aged VG 30

RTFO aged VG 30 is added with different dosages of WEO and the respective variations are compared with the IS 73 recommendations and VG 30, so that the effectiveness of WEO can be verified. Table 4.3 shows the test results of aged and WEO rejuvenated binder. It is evident from below table that WEO have property restoration capacity; when comparing different dosages with VG 30. 3% rejuvenation is found to be the optimum dosage, as that rejuvenated properties are more comparable with virgin VG 30.

Table 4.3: Variation in Physical Properties of RTFO Aged VG 30 due to WEO

Tests	IS 73	Virgin VG 30	RTFO Aged VG 30	RTFO + 2% WEO	RTFO + 3% WEO	RTFO + 4% WEO
Softening Point (ºC)	47 (Min)	53.5	65	59	52.5	45
Penetration (0.1 mm)	45 (min)	45.2	24	35	42.5	48
Elastic Recovery (%)	-	15	4	18	18	18
Viscosity (cP) at 135ºC	350 (min)	453	673	575	460	438

4.3.2.1 Effect of WEO on Softening Point of RTFO Aged VG 30

The Figure 4.1 gave a pictorial representation of variation in softening point of aged binder and its rejuvenation with WEO. Inferences made from the analysis are, when comparing virgin VG 30 with RTFO aged (short term aged) binder there is an increase in softening point, around 21.49 % w.r.t virgin binder. When comparing the role of rejuvenators, 2% and 3% of WEO can improve binder property but 4% WEO failed to meet the code recommendations and virgin binder property. Percentage variation due to rejuvenation are such that 9.23 % decrease in softening point for 2% rejuvenation, 19.23 % decrease in softening point for 3% rejuvenator and 30.76 % decrease in softening point for 4% rejuvenator w.r.t RTFO aged VG 30.

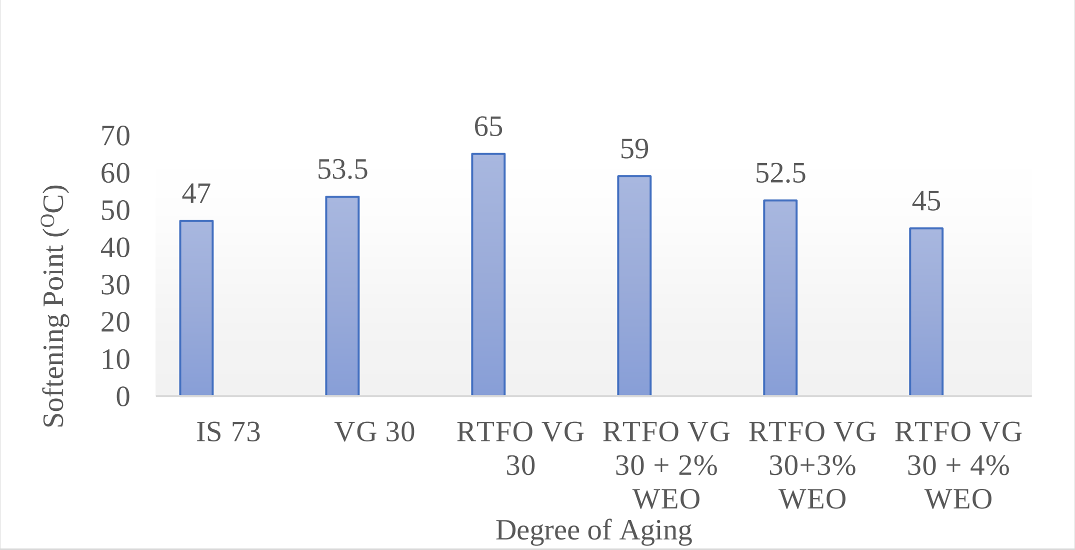

Figure 4.1: Variation in Softening Point due to WEO

4.3.2.2 Effect of WEO on Penetration of RTFO Aged VG 30

From Figure 4.2 shown below there are certain inferences based on the comparison between binder samples. Insights developed from the test results are that only virgin binder and 4% WEO satisfies the code recommendations. Reduction in penetration due to RTFO aging is around 46.9% with respect to virgin binder. Reduction in penetration corresponding to 2% rejuvenation is around 45.83%, 77.08% for 3% and 100% for 4% WEO with respect to RTFO aged VG 30.

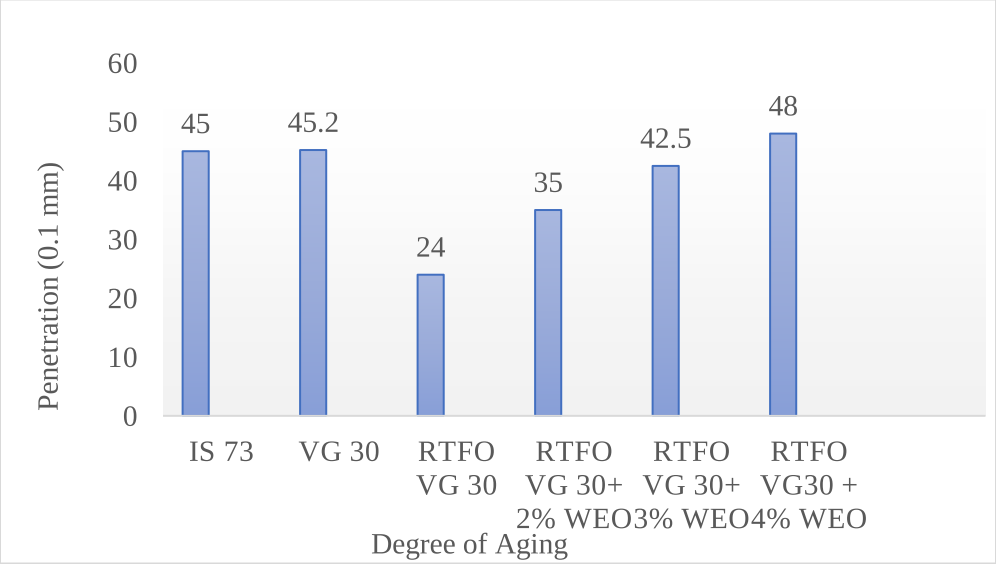

Figure 4.2: Variation in Penetration due to WEO

4.3.2.3 Effect of WEO on Viscosity of RTFO Aged VG 30

Figure 4.3 depicts the variations in viscosity with degree of aging or dosage of rejuvenation. Aged VG 30 samples satisfy the viscosity requirements as per IS 73. There is an increase in viscosity about 48.57% in case of RTFO aged sample with respect to virgin binder. Hence can be stated that rejuvenation is found to be effective in bringing down the viscosity towards virgin binder. When comparing the variation with respect to RTFO aged bitumen 2% rejuvenator can make 14.56% reduction, 3% rejuvenator can make 31.65% reduction and 4% rejuvenator can make 34.92% reduction respectively.

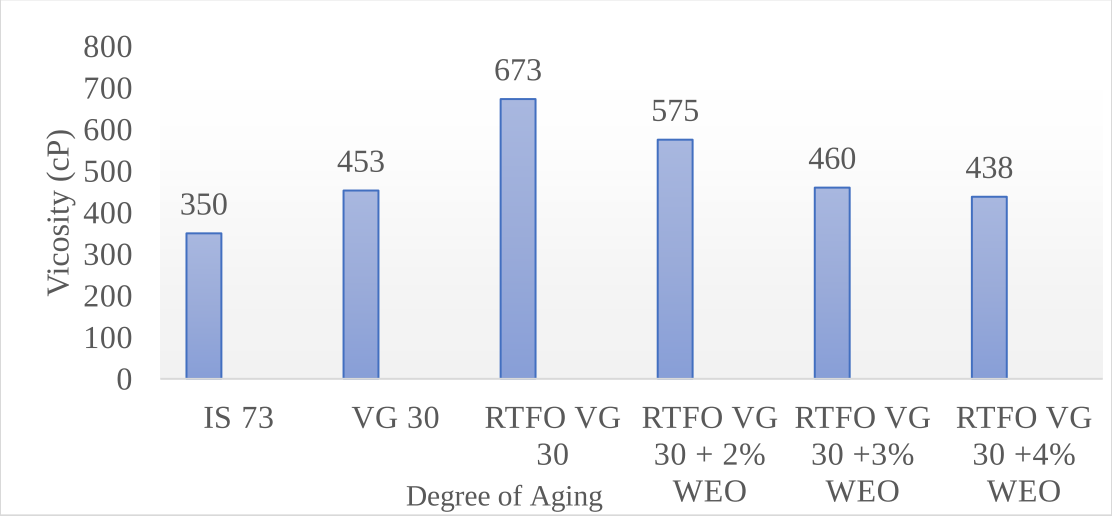

Figure 4.3: Variation in Viscosity due to WEO

4.3.2.4 Effect of WEO on Elastic Recovery of RTFO Aged VG 30

Elastic recovery can be defined as the property which enables the binder to recover its original state from any deformation that happened due to loading. Elastic nature enables the binder to avoid possibilities of permanent deformation. From the results there is a reduction in elastic nature due to short term aging by 73.33% and all dosages of rejuvenation can impart 77.77% increase in elastic recovery. Hence, WEO as a rejuvenator can be effectively used to regain the original state of binder; rejuvenated binder is better than unaged VG 30 and the rejuvenation for each dosage is found to be constant from the laboratory test results. Hence can be concluded that any deformation happened on the binder can be regained by the rejuvenated binder and this will help in increasing the durability of pavement.

4.3.3 Effect of WCO on Physical Properties of RTFO Aged VG 30

Rejuvenation of RTFO aged binder with WCO showed that there are significant improvements in the binder properties. When comparing this with the effect of WEO, WCO is found to be better in restoring properties. Table 4.4 enumerates variations in physical properties of RTFO aged binder under WCO rejuvenation. When comparing the restoration capacity of WCO in different physical properties, 3% dosage is found to be the optimum.

Table 4.4: Variation in Physical Properties of RTFO Aged VG 30 due to WCO

Tests	IS 73	Virgin VG 30	RTFO Aged Binder	RTFO + 2% WCO	RTFO + 3% WCO	RTFO + 4% WCO
Softening Point (°C)	47 (min)	53.5	65	57.5	51	42.5
Penetration (0.1 mm)	45 (min)	45.2	24	38	43.75	49.5
Elastic Recovery (%)	-	15	4	10	15	18
Viscosity (cP) at 135°C	350 (min)	453	673	495	450	410

4.3.3.1 Effect of WCO on Softening Point of RTFO Aged VG 30

Degree of rejuvenation is found to be more in case of WCO when comparing it with the effect of WEO. Considering the changes in softening point there is an increase in softening point of RTFO VG 30 with respect to virgin VG 30 about 21.49 %. Reduction in softening point due to different dosages of WCO are such that 2 % WCO can reduce softening point by 11.54 % with respect to RTFO, 3 % WCO can reduce softening point by 21.53 % with respect to RTFO, 4 % WCO can reduce softening point by 34.62 % with respect to RTFO. Figure 4.4 depicts the pattern of variation in softening point of RTFO aged VG 30 due to different dosages of WCO and its comparison with VG 30 and IS 73 recommendations.

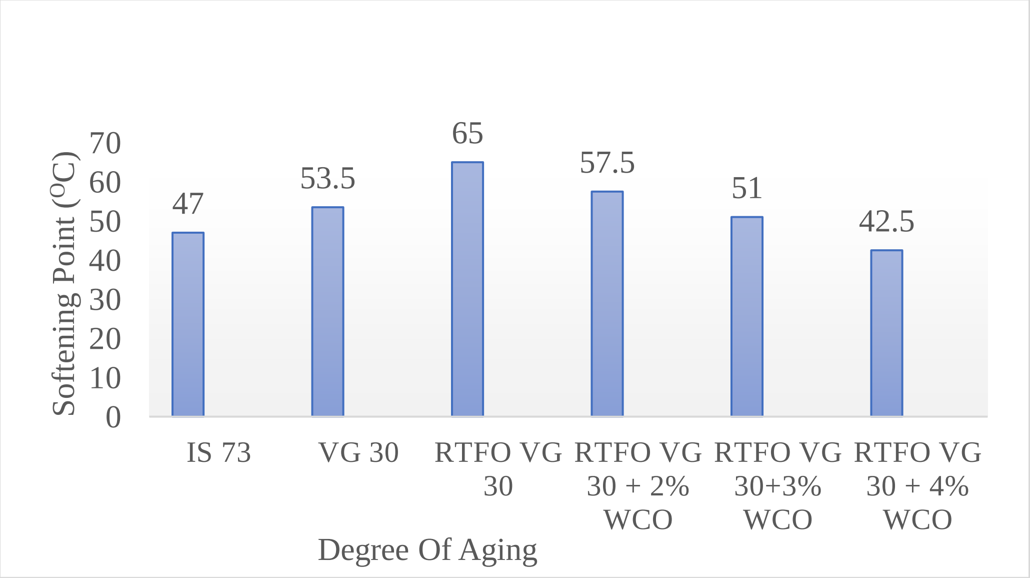

Figure 4.4: Variation in Softening Point due to WCO

4.3.3.2 Effect of WCO on Penetration of RTFO Aged VG 30

Variations in penetration of RTFO aged binder can be explained such that as the dosage of rejuvenator increases penetration also increases. When comparing these values with unaged VG 30, 2% rejuvenation is found to not achieving the requirement and 4% is found to be exceeding the limit. 3% and 4% rejuvenations are approximately nearer to the penetration in VG 30. From Figure 4.5 certain inferences are made such that reduction in penetration of RTFO aged VG 30 with respect to VG 30 is about 46.9%. 2 % WCO can increase penetration by 58.33 %, 3 % WCO can increase penetration by 82.29 %, 4 % WCO can increase penetration by 95.83% with respect to RTFO aged binder.

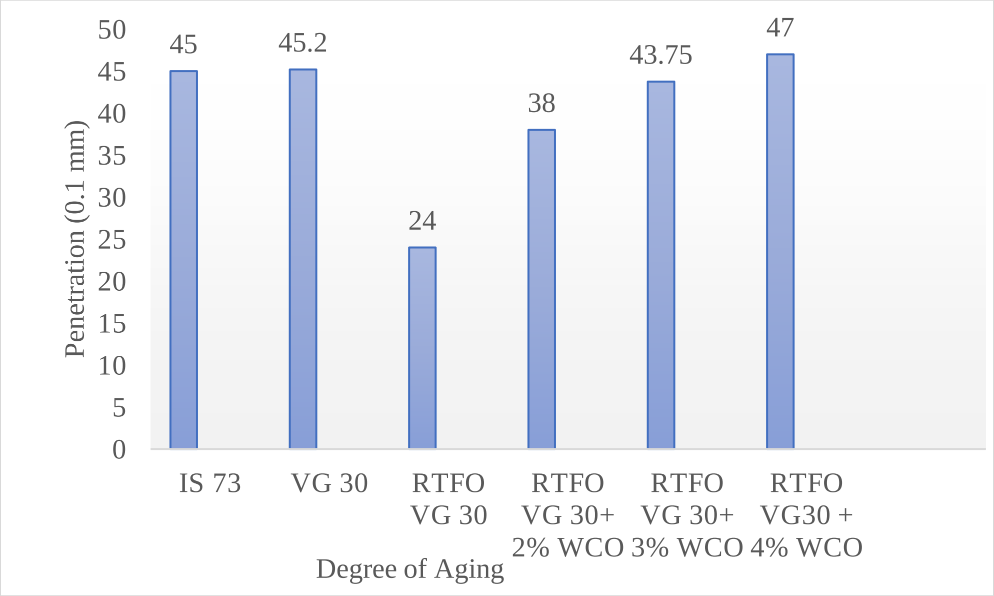

Figure 4.5: Variation in Penetration due to WCO

4.3.3.3 Effect of WCO on Viscosity of RTFO Aged VG 30

Figure 4.6 shows the variation in dynamic viscosity due to different degree of aging and rejuvenation. RTFO aging creates an increase in viscosity of about 48.56% based on VG 30.

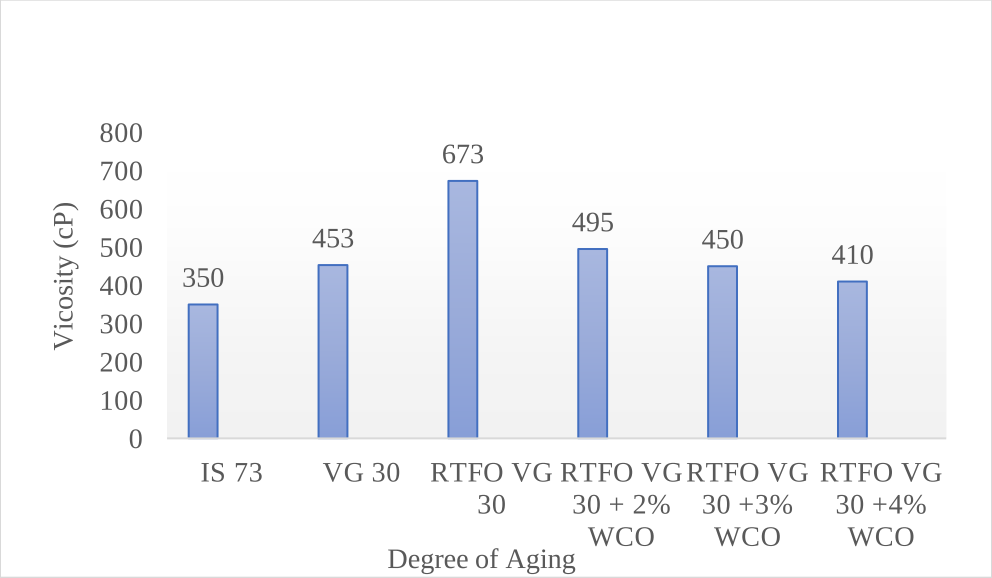

Figure 4.6: Variation in Viscosity due to WCO

Other inferences are such that 2 % WCO can decrease viscosity by 26.45 %, 3 % WCO can decrease viscosity by 33.13 % and 4 % WCO can decrease viscosity by 39.08 % with respect to RTFO.

4.3.3.4 Effect of WCO on Elastic Recovery of RTFO Aged VG 30

From Table 4.4 it can be concluded that WCO can gradually increase the elastic recovery of RTFO aged sample and this will be helpful in recovering the deformations happened due to loading. Due to RTFO aging elastic recovery reduced from 15 to 4, which is around 73.33 %. But WCO rejuvenation results in gradual increase in the property where 2% WCO imparts 60% elastic recovery, 3% impart 73.33% and 4% impart 77.77% of recovery in the specimen. Hence WCO is found effective in restoring the elastic property of aged bitumen.

4.3.4 Comparison Between the Effects of WEO and WCO on RTFO Aged VG 30

From Table 4.3 and 4.4, variations in physical properties of bitumen samples under different rejuvenator dosages are compared with unaged VG 30 and optimum dosage is determined. Laboratory experiments were conducted on RTFO aged binder at 2,3 and 4% rejuvenation with WEO and WCO; results were such that 3% of WEO and WCO are found optimum for rejuvenating RTFO aged VG 30. Table 4.5 includes physical properties of WEO and WCO rejuvenated binder at optimum dosage and certain inferences are made.

Table 4.5: Comparison Between the Effects of WEO and WCO on RTFO Aged VG 30

Tests	Virgin VG 30	RTFO aged VG 30	RTFO aged VG 30+3% WEO	RTFO aged VG 30+3% WCO
Softening Point (°C)	53.5	65	52.5	51
Penetration (0.1 mm)	45.2	24	42.5	43.75
Viscosity (cP)	453	673	460	450
Elastic Recovery (%)	15	4	18	15

When comparing the rejuvenation between WEO and WCO on RTFO aged VG 30, same dosage of WCO can impart a decrease of 1.5°C in softening point, an increase in penetration by 1.25mm a decrease in viscosity by 10cP with respect to WEO and reduction in elastic recovery by 3%. Hence WCO can impart better rejuvenation on RTFO aged binder. Higher content of fatty acid in waste cooing oil is considered as the reason behind the efficiency of waste cooking oil.

4.3.5 Effect of WEO on Physical Properties of RAP VG 30

Table 4.6 and Table 4.7 shows the variation in physical properties of RAP and rejuvenation at different percentages of WEO and WCO respectively. From both tables results follows pattern as in case of RTFO aged binder and its rejuvenation. From both table 5% WEO and 4% WCO are found to have effective rejuvenation. Here WEO imparts equal amount of elastic recovery with the three dosages but WCO is gradually increasing the elastic recovery property. This may be due to the presence of lubricants in WEO that the initial dosage itself can impart 18% of elastic recovery; which is achieved by WCO only at 5% dosage.

Table 4.6: Variation in Physical Properties of RAP VG 30 due to WEO

Tests	IS 73	Virgin Binder	Recovered Binder (RAP)	RAP + 3% WEO	RAP + 4% WEO	RAP+ 5% WEO
Softening Point (°C)	47 (min)	53.5	78	66	62.5	54
Penetration (0.1 mm)	45 (min)	45.2	8.3	24	37	42
Elastic Recovery (%)	-	15	Test failed	18	18	18
Viscosity (cP) at 135°C	350 (min)	453	748	648	573	465

Considering softening point, 3% WEO impart a reduction of 15.38%, 4% impart 19.87% and 5% impart 30.76 % respectively. Effect on rejuvenation on penetration is such that there are increase in penetration by 2.89 times for 3% WEO, 4.45 times for 4% and 5 times for 5% WEO respectively. Comparing elastic limit, it remains a constant value of 20% at all the dosages of WEO with respect to virgin VG 30, but viscosity is having gradual reduction with respect to increase in dosage. For

3% reduction in viscosity is around 13.36%, for 4% and 5%, the reduction is 23.39% and 37.83% respectively. Comparing the variations in properties with respect to dosage, 5% WEO is found out to be the optimum.

4.3.6 Effect of WCO on Physical Properties of RAP VG 30

From Table 4.7 certain inferences are made such that softening point can be reduced by 20.51% for 3% dosage, 28.85 % for 4% and 41.67 % for 5% dosage respectively. In case of penetration there is 3.55 times, 5.12 times, 5.78 times increase with respect to 3%, 4% and 5% WCO respectively. Elastic recovery with respect to VG 30 is such that 3% rejuvenation impart a reduction of 33.33% for 3% WCO, 20% increase for 5% WCO and there is no change in elastic recovery for 4% dosage. Variation in viscosity can be concluded as decrease by 17.11%, 22.73%, 45.19% with respect to 3%, 4% and 5% WCO respectively.

Table 4.7: Variation in Physical Properties of RAP VG 30 due to WCO

Tests	IS 73	Virgin Binder	Recovered Binder	RAP + 3% WCO	RAP + 4% WCO	RTFO + 5% WCO
Softening Point (^oC)	47 (min)	53.5	78	62	55.5	45.5
Penetration (0.1 mm)	45 (min)	45.2	8.3	29.5	42.5	48
Elastic Recovery (%)	-	15	Test failed	10	15	18
Viscosity (cP) at 135	350 (min)	453	748	620	578	410

4.4 COMPARISON BETWEEN CHEMICAL PROPERTY ANALYSIS ON VG- 30

4.4.1 Identifying the Functional Groups in VG 30, WEO and WCO

Identifying the functional groups in VG 30, waste engine oil and waste cooking oil is to check the compatibility between the three materials so that they can be blended, to compliment as pavement materials, hence to pave the way for sustainable development. From Figure 4.7, the spectra obtained from FTIR spectroscopy for VG 30, WEO and WCO, there are functional groups in-common between these materials. Formation of functional groups are identified from the peaks formed in the spectra and the area of peak centered around the fingerprint wavelength is used to calculate the aging indices. Carbonyl index and sulfoxide index are considered as the measure of long term and short-term aging respectively. FTIR spectra is drawn using the Origin software and area calculation for the determination of aging index is also obtained from the software. Figure 4.7 shows the stacked graphs of VG 30, WEO and WCO for functional groups identification and Table 4.8 includes functional groups and the corresponding wave number for VG 30 and rejuvenators.

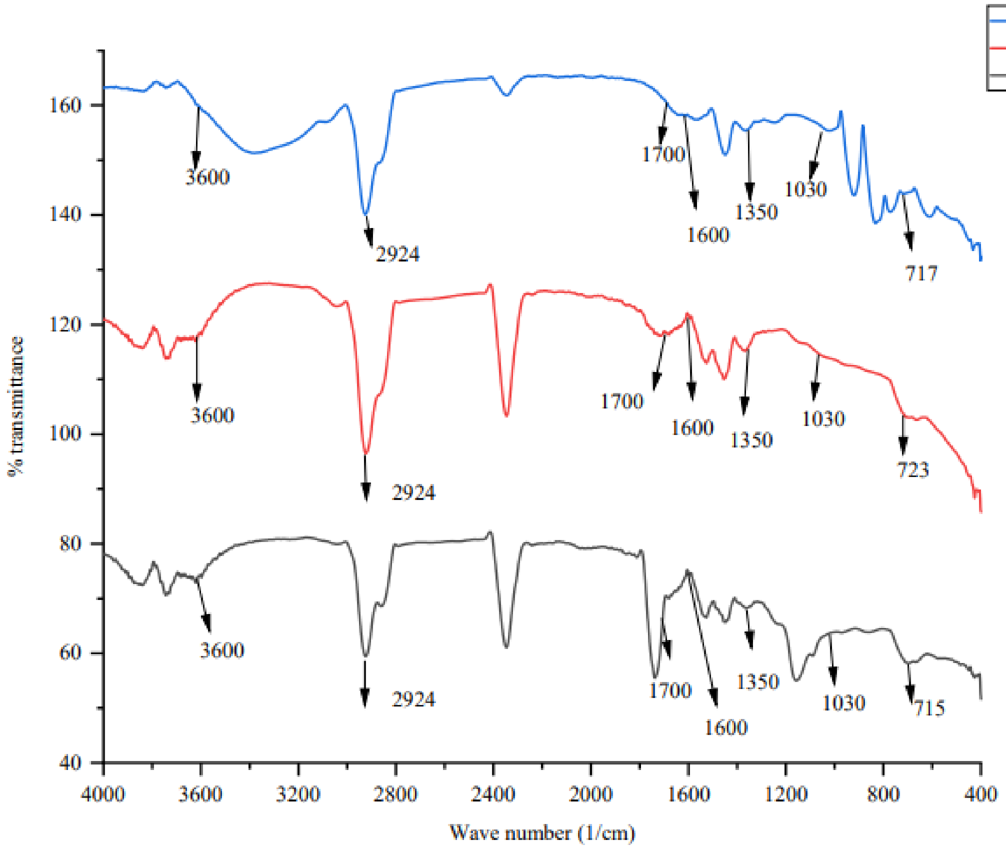

Figure 4.7: Stacked Graphs of VG 30, WEO and WCO for Functional Group Identification

From the spectra, it can be identified that there are peaks of functional groups and characteristic compounds. But functional groups present at fingerprint wavelength have changes in intensity and area of the peak. This is considered to be sufficient in calculating the aging in binder. From Table 4.8 it is clear that binder and rejuvenators are having the same functional groups at same wave number range. The type of interaction of molecular bonds with the infrared radiations are also similar in nature. Hence can be concluded that binder and rejuvenators can be behave similarly as pavement material.

Table 4.8 Functional Groups and Corresponding Wave Number for VG 30 and Rejuvenators.

Wave number and functional groups for VG 30 (Nivitha et al., 2016)	Wave number and functional groups for WEO (Wolak et al., 2016)	Wave number and functional groups for WCO (Wan et al., 2016)
3641: Hydroxyl group O=H	3600: Hydroxyl group O=H	3700- 3500: Hydroxyl group O=H
3000-2800: Asymmetric and symmetric stretches of C-H in CH_2 and CH_3 2800-2700: Carboxylic acid formation	2924-2852: Asymmetric and symmetric stretches of C-H in CH_2 and CH_3 2800-2700: Carboxylic acid formation	3000-2800: Asymmetric and symmetric stretches of C-H in CH_2 and CH_3 2800-2700: Carboxylic acid formation
1700: Carbonyl compounds, C=O	1743: Carbonyl compounds, C=O	1660-1800: Carbonyl compounds, C=O
1032: Sulfoxides, S=O	1100: Sulfoxides, S=O	1150: Sulfoxides, S=O

4.4.2 Comparison Between Unaged and Aged VG 30

FTIR spectra have similarities between three types of aging conditions as shown in Figure 4.8. Spectra contains common characteristic functional groups but there are variations in the peaks in terms of amplitude and area. This can be interpreted as the difference in degree of aging occurred in bitumen. Figure 4.9 shows the area of peaks calculated, and as per studies area of peaks corresponding to carbonyl compounds (wave number between 1678-1720 cm^{-1}), sulfoxides (wave number between 1010-1043 cm^{-1}), aliphatic (wave number between 1350-1510 cm^{-1}), aromatic (wave number between 1535-1625 cm^{-1}), and long chains (wave number between 715-733 cm^{-1}) are represented in the figure.

Origin 2023 software is used to draw the FTIR spectra and there are provisions in the software to integrate the area between the required wave numbers. This provision is used for the calculation of aging index. Carbonyl index, sulfoxide index, aromatic index, aliphatic index and long chain index are used to quantify different degree of aging and other indicator parameter representing the chemical reaction like aromatization as part of aging. Figure 4.9, Figure 4.10 and Figure 4.11shows the area under FTIR spectra for calculating aging indices of VG 30, RTFO aged VG 30 and RAP

VG 30 respectively. There is relative increase or decrease between the indices that can be compared to interpret the extend of aging and the reason behind it. Table 4.9 includes aging indices for RTFO aged VG 30 and its rejuvenated samples.

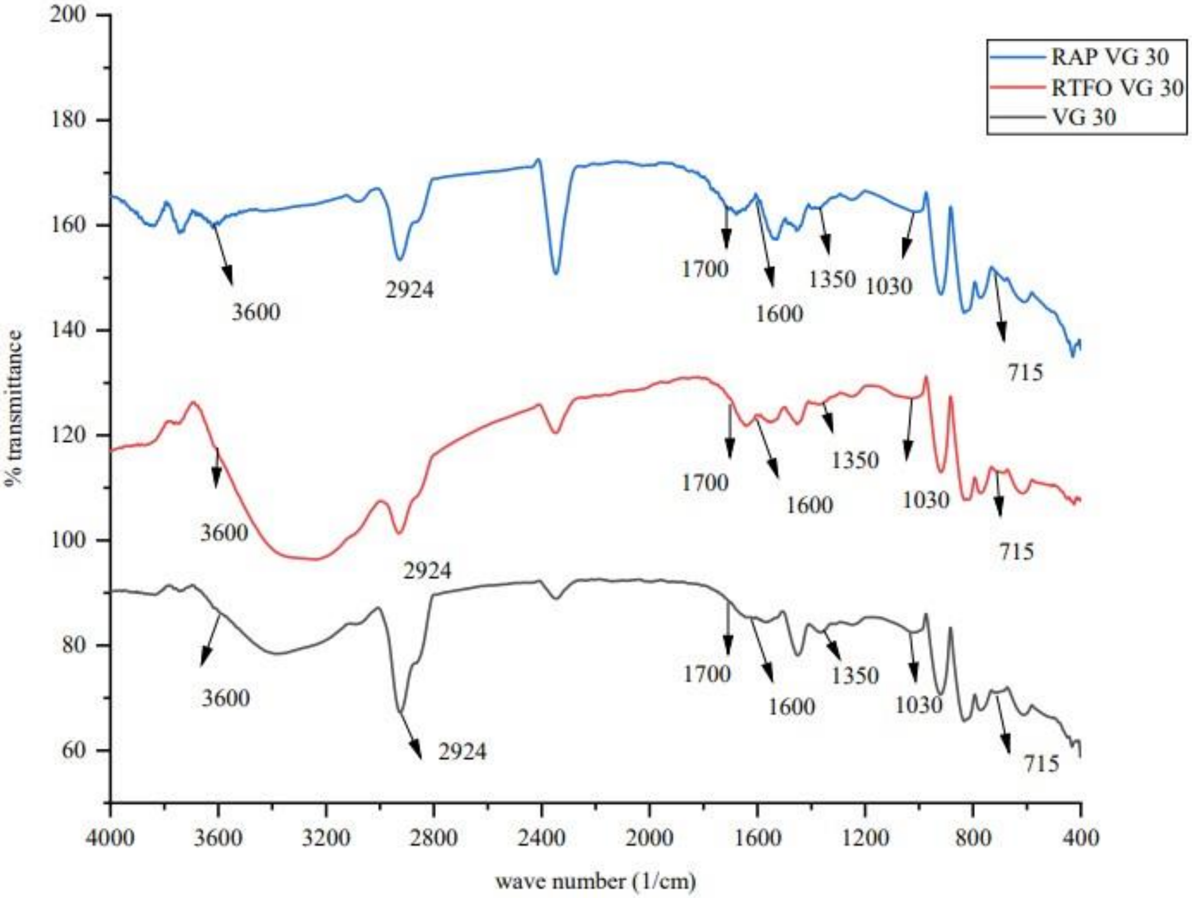

Figure 4.8: FTIR Spectra Comparing the Aging in VG 30

From Table 4.9, There is sulfoxide index for virgin VG 30 even though it is considered unaged, this is because of the conversion of elemental sulphur by oxidation during production stage. Sulfoxide index (SI) of VG 30 is less in comparison with RTFO aged VG 30 because RTFO aged binder is subjected to rapid rate of oxidation, hence the value is higher. But SI value of VG 30 is slightly higher than RAP VG 30 this is because after attaining some degree of aging there is decomposition of sulfoxides and both formation and decomposition of sulfoxides occur simultaneously. Carbonyl index for VG 30, RTFO aged VG 30 and RAP VG 30 are increasing gradually as degree of aging increases. Increase in carbonyl index is due to the reaction of oxygen with per- hydroaromatic ring to form hydro-peroxides. These hydroperoxides initiates faster production of ketones and sulfoxides. Aromatic index is considered as an indicator of aromatization of per-hydro aromatic ring to make it stable by cluster formation and reduction in viscosity. This phenomenon contributes to initial shoot up of viscosity in addition to oxidation in bitumen. With increase in aromatisation there is a simultaneous decrease on aliphatic compound due to chemical reaction and the same long chain compounds.

Table 4.9: Comparison Aging Indices of Unaged, RTFO Aged and RAP VG 30

Bitumen type	Sulfoxide Index $A_{1010-1043}/\sum A$	Carbonyl Index $A_{1678-1725}/\sum A$	Aliphatic Index $A_{1350-1510}/\sum A$	Aromatic Index $A_{1535-1625/}\sum A$	Long chain Index $A_{715-733/}\sum A$
VG 30	0.019	0.016	0.674	0.181	0.035
RTFO aged VG 30	0.077	0.099	0.58	0.24	0.008
RAP VG 30	0.018	0.273	0.344	0.338	0.027

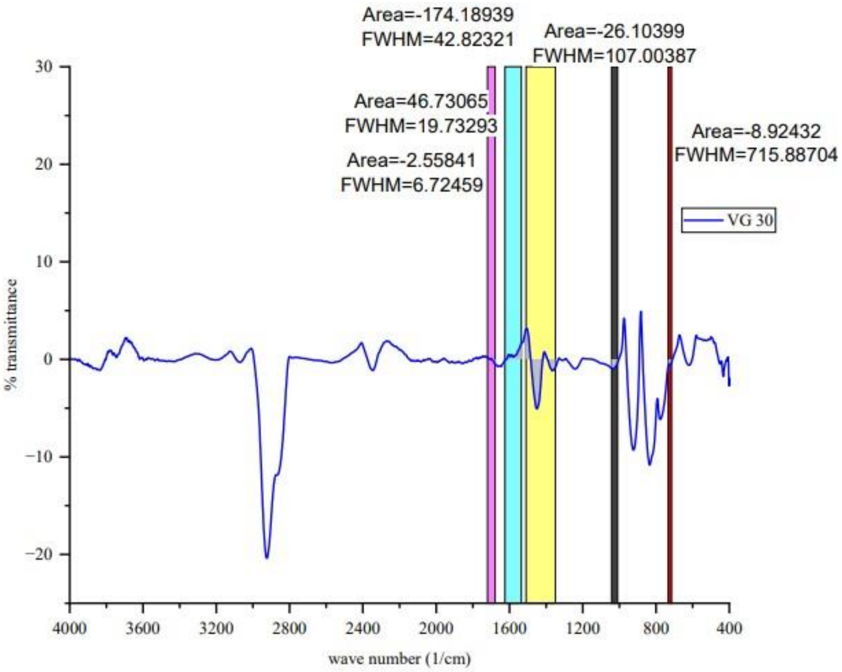

Figure 4.9: Area Under Functional Group Peaks for Aging Index Calculation- VG 30

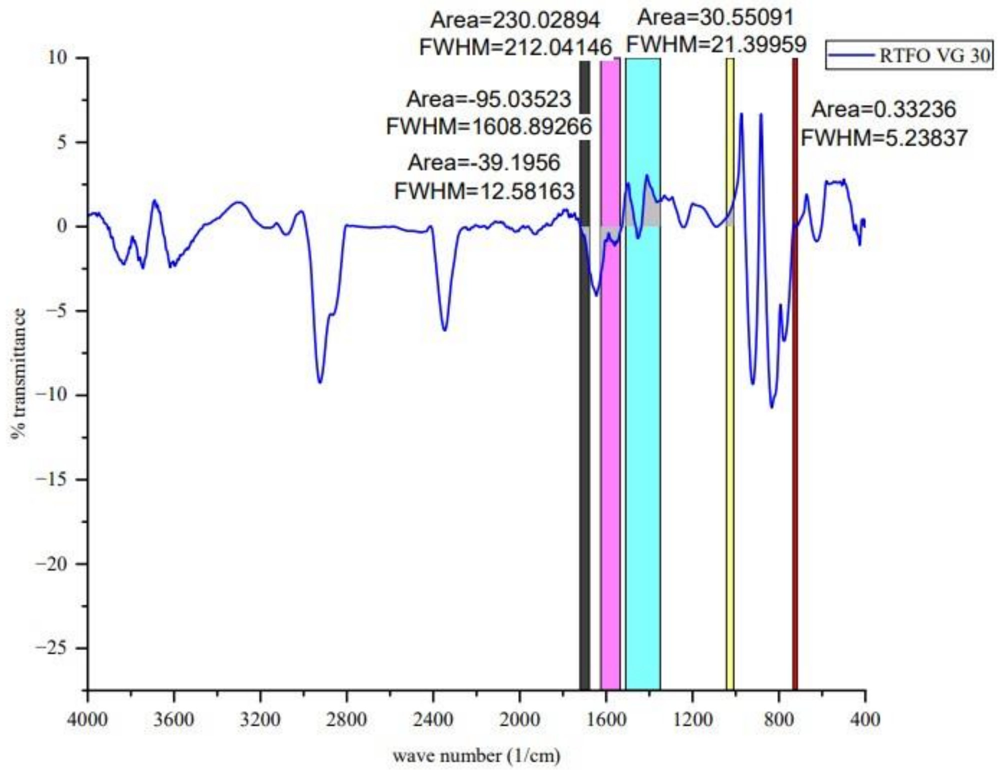

Figure 4.10: Area Under Functional Group Peaks for Aging Index Calculation- RTFO aged VG 30

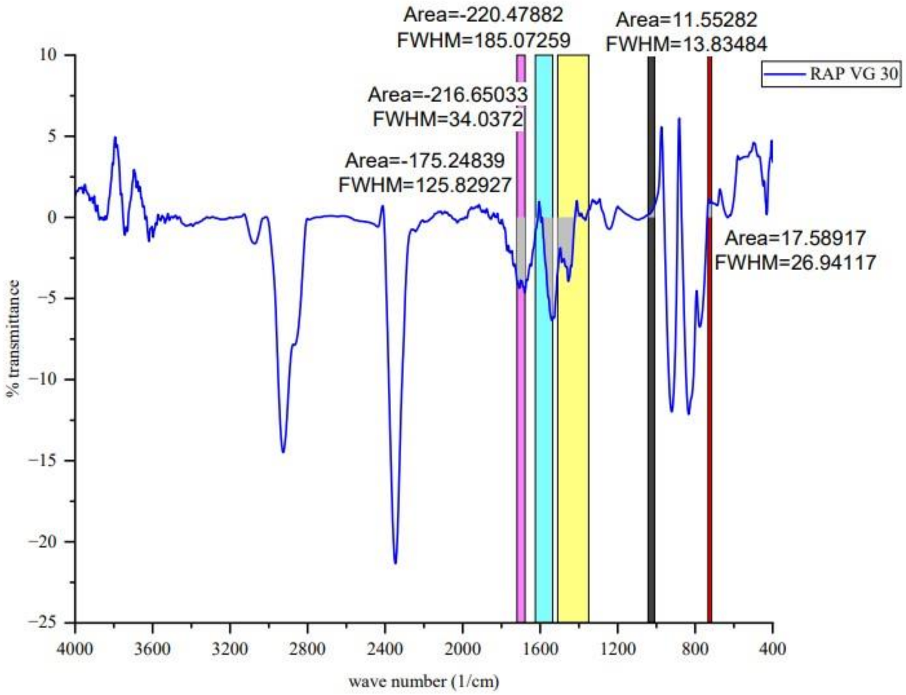

Figure 4.11: Area Under Functional Group Peaks for Aging Index Calculation- RAP VG 30

4.4.3 Comparison Between Effect of Rejuvenators on RTFO Aged Samples

There are certain similarity and differences between the spectra of VG 30, RTFO aged VG 30, RTFO rejuvenated with 3% WEO and RTFO rejuvenated with 3% WCO. But the calculated indices have significant differences. Figure 4.12 Compares the effectiveness of WEO and WCO on RTFO aged VG 30 and Table 4.10 compares the aging indices of RTFO aged VG 30 rejuvenated with WEO and WCO.

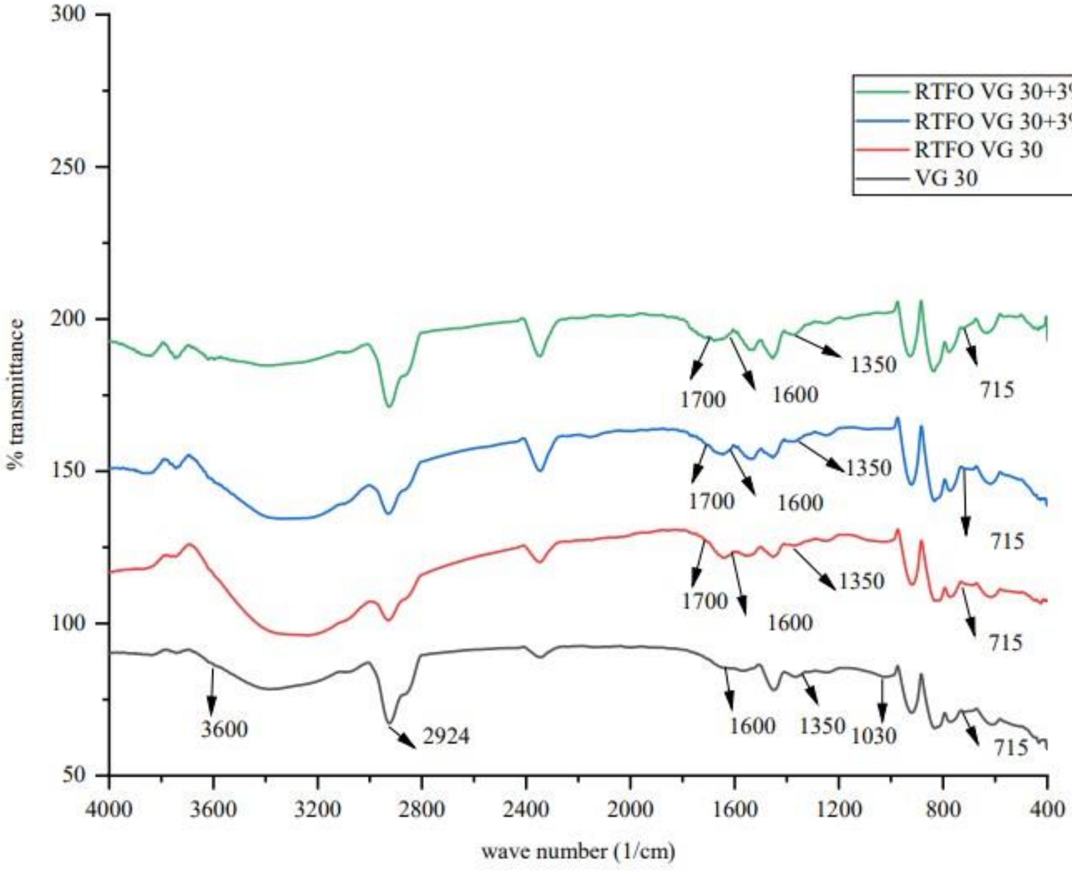

Figure 4.12: Comparison Between Effectiveness of WEO and WCO on RTFO aged VG 30

From Table 4.10 it can be stated that WCO performs better than WEO at same dosage, but in case of physical properties both were having an optimum performance. In chemical property analysis WCO performs well in the reduction of both SI and CI values and WEO is increasing the aging index and can be substantiated that WEO is not able to reduce the aging during blending of rejuvenators with the binder. Rejuvenators are effective in maintaining the complimentary relation between aliphatic and aromatic indices, when aromatic index increase, aliphatic should decrease.

This is achieved in the above case. Long chains are compounds with four or more carbon and the same pattern of variation is obtained here also

Table 4.10: Comparison of Aging Indices of RTFO aged VG 30 with WEO and WCO

Bitumen type	Sulfoxide Index $A_{1010-1043}/\sum A$	Carbonyl index $A_{1678-1725}/\sum A$	Aliphatic index $A_{1350-1510}/\sum A$	Aromatic index $A_{1535-1625}/\sum A$	Long chain index $A_{715-733}/\sum A$
VG 30	0.019	0.016	0.674	0.181	0.035
RTFO aged VG 30	0.077	0.099	0.58	0.24	0.008
RTFO + 3% WEO	0.099	0.208	0.655	0.038	0.001
RTFO + 3% WCO	0.016	0.032	0.424	0.532	0.010

4.4.4 Comparison Between Effect of Rejuvenators on RAP VG 30

From Table 4.11 and Figure 4.13 it can be said that there is similar pattern of variation among various indices and the effect of rejuvenators as mentioned in previous cases. There is an increase in SI and CI values with aging and proportional reduction in those indices with the addition of rejuvenators. Figure 4.13 shows stacked FTIR spectra of VG 30, RAP binder and its rejuvenated samples. It is found that the sulfoxide and carbonyl index increase with degree of aging and decreases with rejuvenation. It is evident that both WEO and WCO can reduce SI and CI values considerably from RAP VG 30. Comparing the effect of optimum dosages of WEO and WCO on RAP binder 5% WEO is found comparatively efficient in reducing the degree of aging in terms of chemical properties. In relation with aging there is an increase in aromatic index due to aromatization and corresponding reduction in aliphatic compounds, as aliphatic compounds reduce due to aromatization. Long chain index is associated with the variations in aliphatic index.

Table 4.11: Comparison of Aging Indices of RAP VG 30 with WEO and WCO

Bitumen type	Sulfoxide Index $A_{1010-1043}/ \sum A$	Carbonyl index $A_{1678-1725}/ \sum A$	Aliphatic index $A_{1350-1510}/ \sum A$	Aromatic index $A_{1535-1625}/ \sum A$	Long chain index $A_{715-733}/ \sum A$
VG 30	0.019	0.016	0.674	0.181	0.035
RAP VG 30	0.018	0.273	0.344	0.338	0.027
RAP + 5% WEO	0.014	0.019	0.742	0.207	0.018
RAP + 4% WCO	0.032	0.211	0.375	0.152	0.231

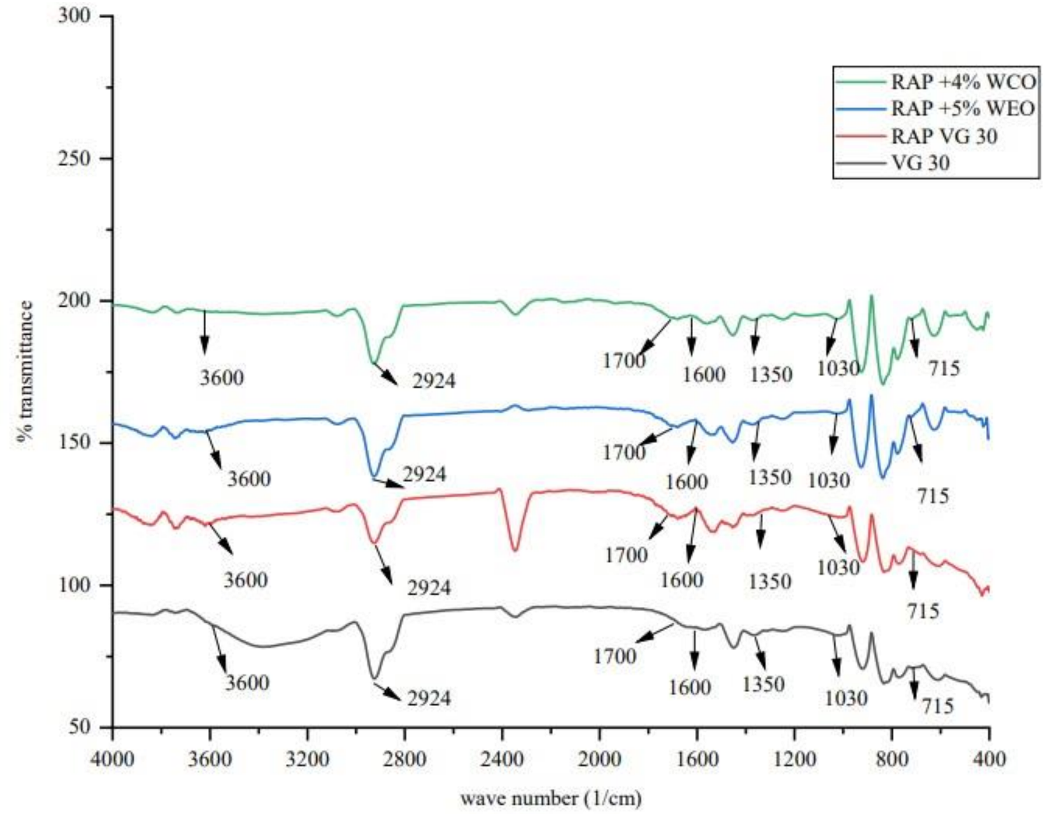

Figure 4.13: Comparison Between Effectiveness of WEO and WCO on RAP VG 30

4.5 COMPARISON OF RHEOLOGICAL PROPERTIES OF VG 30

Different samples of VG 30 are subjected to a sequential testing under frequency sweep and linear amplitude sweep to simulate different loading cycles and its magnitude, under two sets of temperature. The temperature considered is 60 degree and 40 degrees Celsius, which are the maximum pavement temperatures. DSR of Anton Paar MCR 302specification is used to conduct the material testing. LAST test is conducted as per AASHTO TP 101-14, where 8mm diameter 2mm gap geometry is used.

4.5.1 Comparison Between Frequency Sweep Test Results at 40°C and 60°C

4.5.1.1 Variation in Complex Shear Modulus with Frequency

In FS test binder at different aged condition is tested at different temperature, to have a comparison between the variation in complex modulus which is considered as the measure of material stiffness. Frequency sweep simulates the variation in travel speed of vehicle. Therefore, FS test is meant to study the variation in G* value with temperature change and increasing vehicular speed or a greater number of wheel loads passing a section. Figure 4.14 and Figure 4.15 represents the variation in G* value with 40 and 60 degrees Celsius respectively.

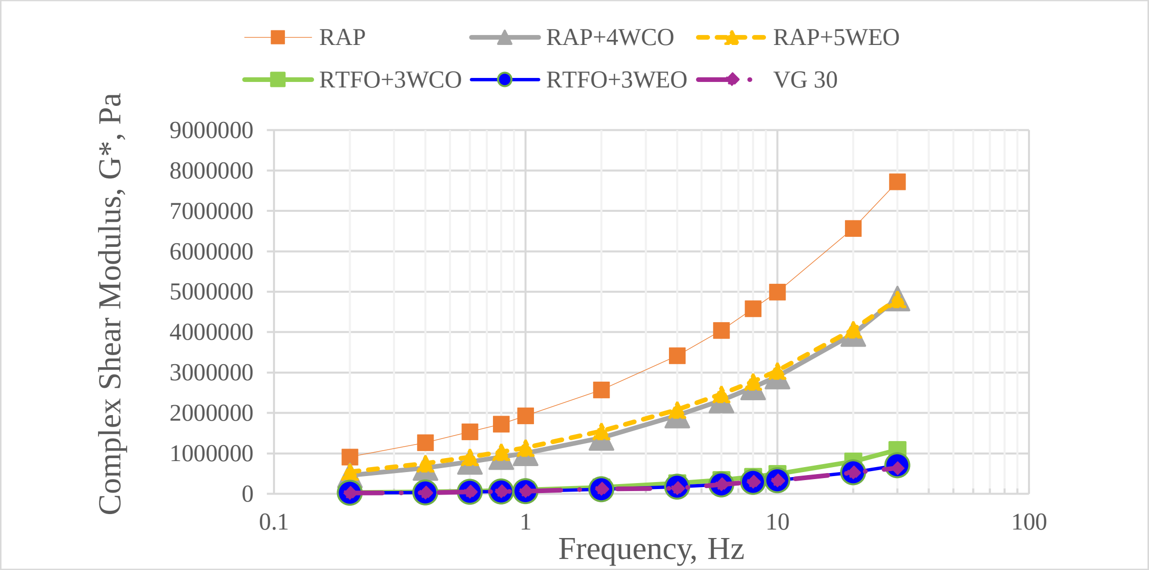

Figure 4.14: Variation in Complex Shear Modulus with Frequency at 40°C

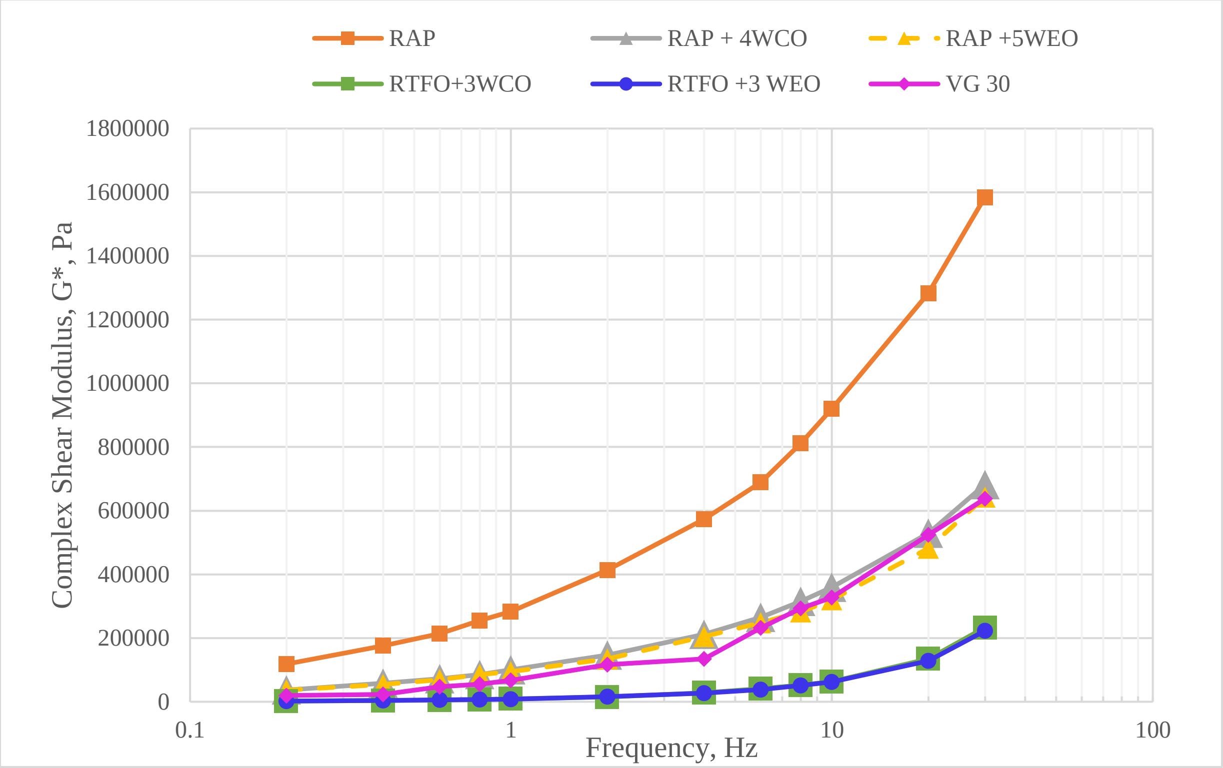

Figure 4.15: Variation in Complex Shear Modulus with Frequency at 60°C

From Figure 4.14, it can be stated that as frequency increases complex shear modulus also increases, which indicates an increase in stiffness of material when subjected to greater number of wheel loads. This can be considered as a measure of aging. Also, G* increases when degree of aging increases. For the same frequency, as aging increases complex shear modulus value also increases. Considering the degree of rejuvenation, comparing with VG 30, RAP is having the highest G* value followed by RAP +4 %WCO and RAP+ 5 %WEO with similar property, then RTFO+ 3%WCO and least value of G* is for RTFO+3% WEO and VG 30. All the four rejuvenated samples fall between RAP and VG 30, but rheological similarity is between RTFO with rejuvenated samples and VG 30.

When comparing Figure 4.15 with Figure 4.14, it can be said that for the same frequency range as temperature increases effect of rejuvenation on RTFO cum rejuvenated binders fall out of the limit of VG 30; where RAP cum rejuvenated samples is merged with VG 30 and falls below RAP binder. This may be because of rise in temperature from 40 to 60 degree Celsius. From both figures, G* value increases with frequency because of increase in asphaltene/maltene ratio due to aging.

4.5.1.2 Variation in Phase Angle with Frequency

In rheology phase angle (δ) is defined as an indicator of visco-elastic nature of binder. It is defined as the time lag between maximum shear stress and shear strain and its value varies between 0 to 90 degrees. Purely viscous material has phase value 90 and purely elastic material have phase value zero degree. Figure 4.16 and Figure 4.17 shows the variation in phase angle of unaged, aged and rejuvenated samples subjected to varying frequency and temperature. In contrary to G* value, δ decreases with increase in frequency and relatively less aged binder is having higher δ value. During all the frequency variations phase angle value lies between zero to 90 degrees which shows that all the binder samples possess visco elastic nature. At 40ºC, VG 30 and RTFO cum rejuvenated samples merged together; RAP and RAP cum rejuvenated samples having similar pattern of variation. At 60ºC there are distinct pattern of variation between the samples and at 10 Hz and 20 Hz frequency some samples possess same value for δ; then decreases with frequency as in case of 40ºC. Variation in phase angle is due to reduction in maltene phase which can influence the fluidity of binder.

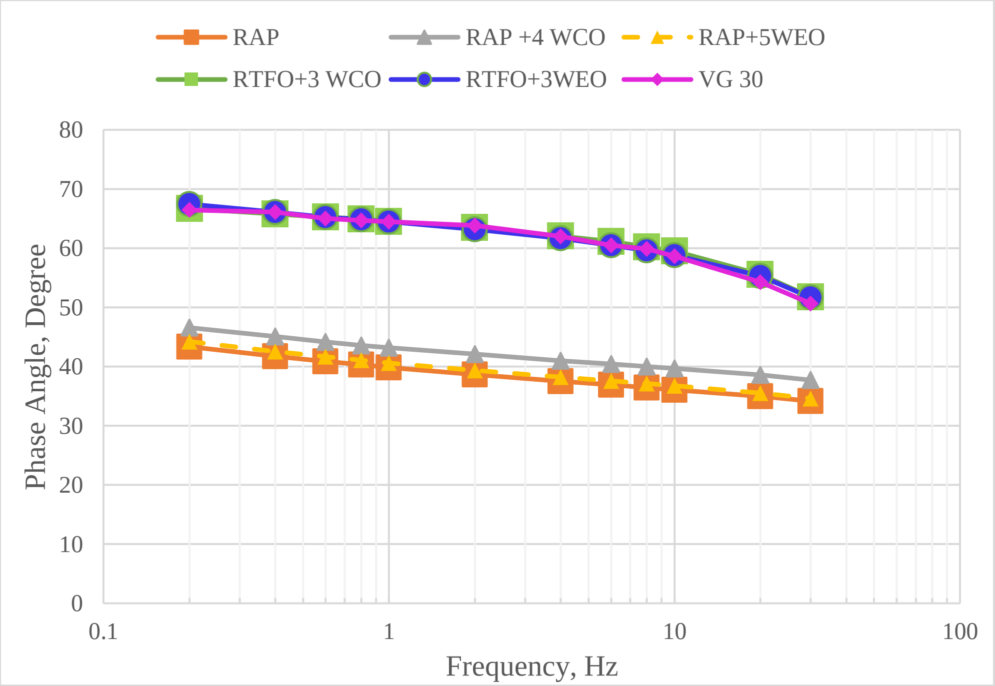

Figure 4.16: Variation in Phase Angle with Frequency at 40ºC

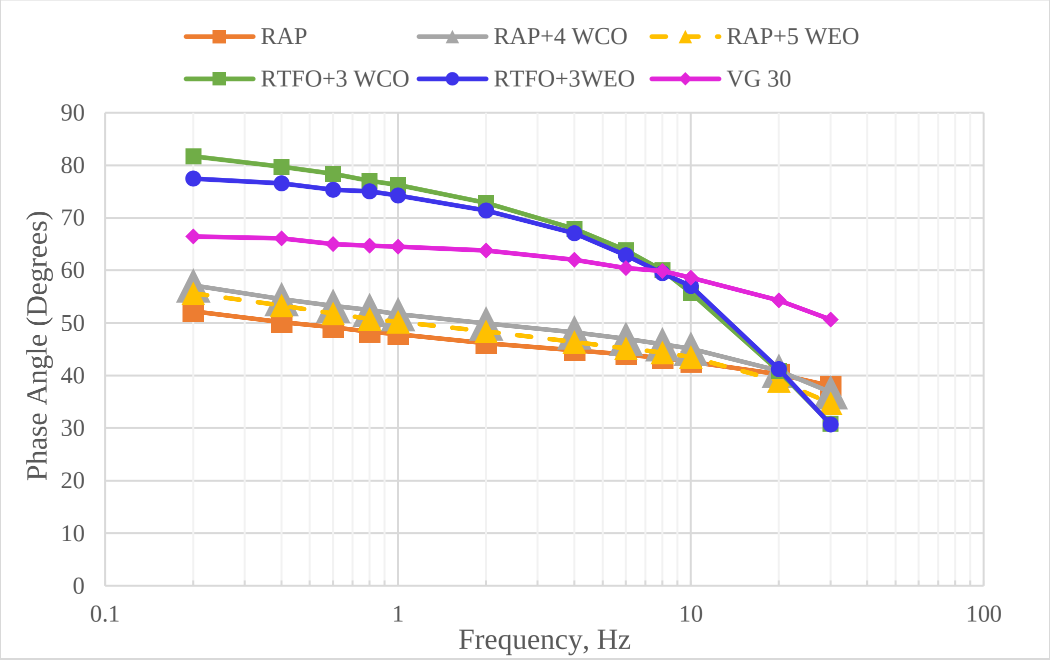

Figure 4.17: Variation in Phase Angle with Frequency at 60ºC

4.5.1.3 Variation in Rutting Parameter with Frequency

In rheology rutting parameter (G*/sinδ) of bituminous binder is considered as the resistance to rutting that it can offer against any permanent deformation due to loading or at high temperature. This can be contributed by the material stiffness. This section deals with the variation in rutting parameter with variation in frequency and temperature; this property being a structural and functional criterion requires greater importance. Figure 4.18 and Figure 4.19 shows the above-mentioned changes at 40ºC and 60ºC respectively. Even though stiffness is the key factor that contributes to rutting resistance, over stiffness makes the pavement to get cracked. Hence rejuvenators are expected to restore the properties comparable to VG 30 and RTFO cum rejuvenated binders are found similar to that of VG 30. At 40ºC there is an increase in rutting resistance with frequency, since higher number of wheel loads imparts hardness to binder; but the rate of variation is gradual and smooth in nature. In case of 60ºC, all the samples except RAP possess lowest level of resistance which is a huge reduction compared to that at 40ºC. Even RAP at 60ºC is having a maximum rutting resistance (around 2500000 Pa) which is equal to the minimum rutting resistance (around 2000000 Pa) at 40°C. Increase in maltenes due to rejuvenation and increase in temperature are the key factors that can negatively influence rutting parameter.

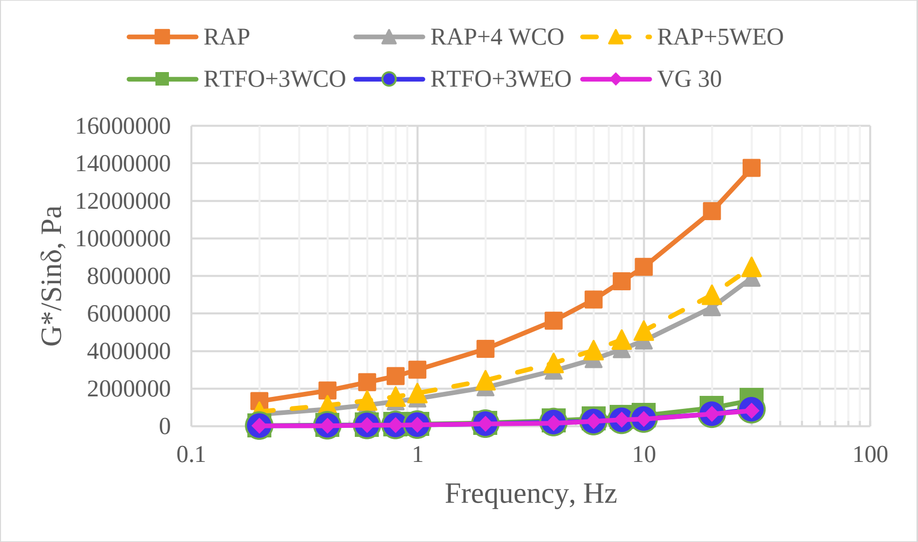

Figure 4.18: Variation in Rutting Parameter with Frequency at 40°C

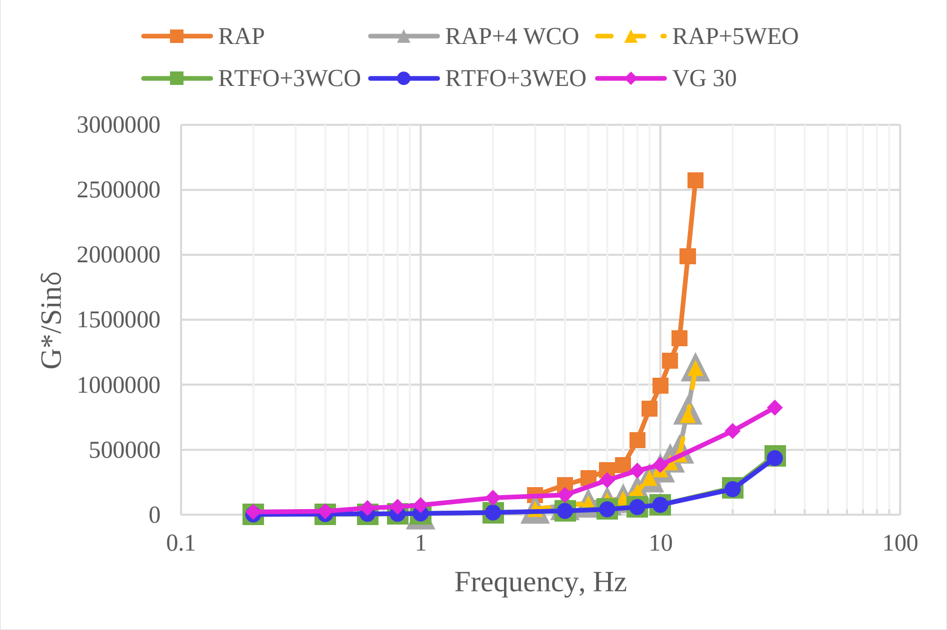

Figure 4.19: Variation in Rutting Parameter with Frequency at 60°C

4.5.1.4 Variation in Fatigue Parameter with Frequency

Fatigue parameter refers to the fatigue damage happened to the binder due to factors influencing aging. It is expressed as G*sinδ, this is considered as the response towards intermediate pavement temperature whereas rutting is considered as high temperature resistance of binder. Figure 4.20 and Figure 4.21 represents the variation of fatigue behaviour with respect to frequency. Fatigue parameter of RAP cum rejuvenators and RTFO cum rejuvenators fall between that of RAP and VG 30. Rejuvenated RAP binders are comparatively stiffer than rejuvenated RTFO aged binders, hence rejuvenators are preferable at 40ºC temperature. At 60ºC fatigue behaviour of all the rejuvenated sample falls below VG 30, that may help in reducing the fatigue crack but there are chances of rutting failure due to lack of stiffness. Since high temperature can adversely affect rutting parameter, reduction in fatigue parameter is not advisable because fatigue and rutting are inversely related. Also, rejuvenators are found effective in reducing G*sinδ at higher temperature, there are significant difference in the pattern of variation and the magnitude of extreme values achieved by the sample. It can also be stated that increase in stiffness and reduction in adhesion between bitumen and aggregate due to aging leads to fatigue damage.

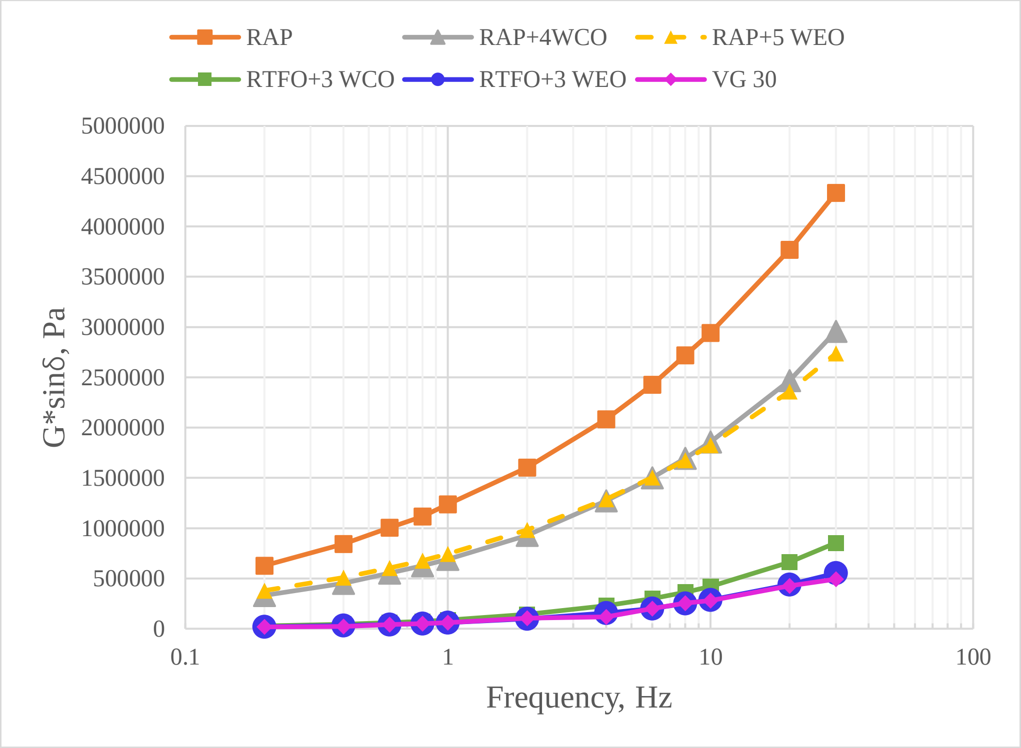

Figure 4.20: Variation in Fatigue Parameter with Frequency at 40ºC

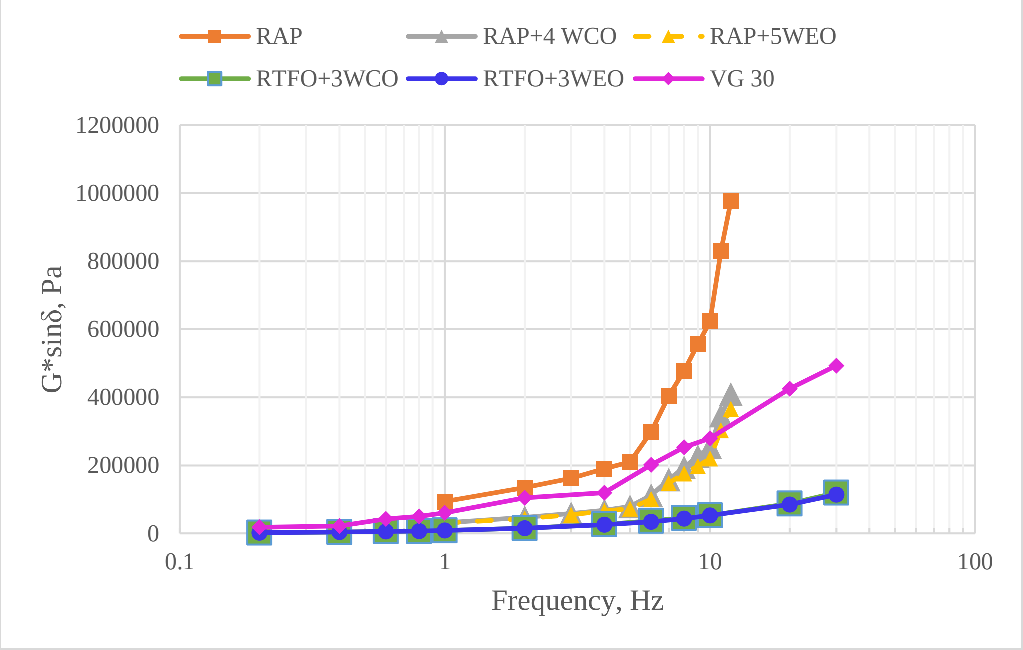

Figure 4.21: Variation in Fatigue Parameter with Frequency at 60°C

4.5.2 Comparison Between Linear Amplitude Sweep Test at 40°C and 60°C

LAS test is conducted at required temperature using oscillatory shear and strain-controlled mode; at a constant frequency of 10 Hz. Continuous oscillatory strain sweeps with load increasing linearly from zero to 30% over the range of 3100 cycles of loading. Shear strain and stress at the peak are recorded at every 10 load cycles (1 sec) along with the magnitude of phase angle, δ (degree) and complex shear modulus, G* (Pa).

4.5.2.1 Variation in Complex Shear Modulus with Change in Time

Figure 4.22 and Figure 4.23 represents the variation in G* value with respect to time (no: of cycles) at 40°C and 60°C respectively. RAP is having highest G* value and VG 30 is having the least with other samples varies in different rate based on the degree of aging. From Figure 4.22, RAP +4% WCO continues till 3000 cycles and all other samples loses their G* value before 3000 cycles or 300 s of loading. Considering degree of aging, relative increase in asphaltenes is the reason for increase in G* value and rejuvenators are found effective in reducing stiffness by increasing the maltene phase, still 4% WCO provides minimum G* value under maximum loading cycle.

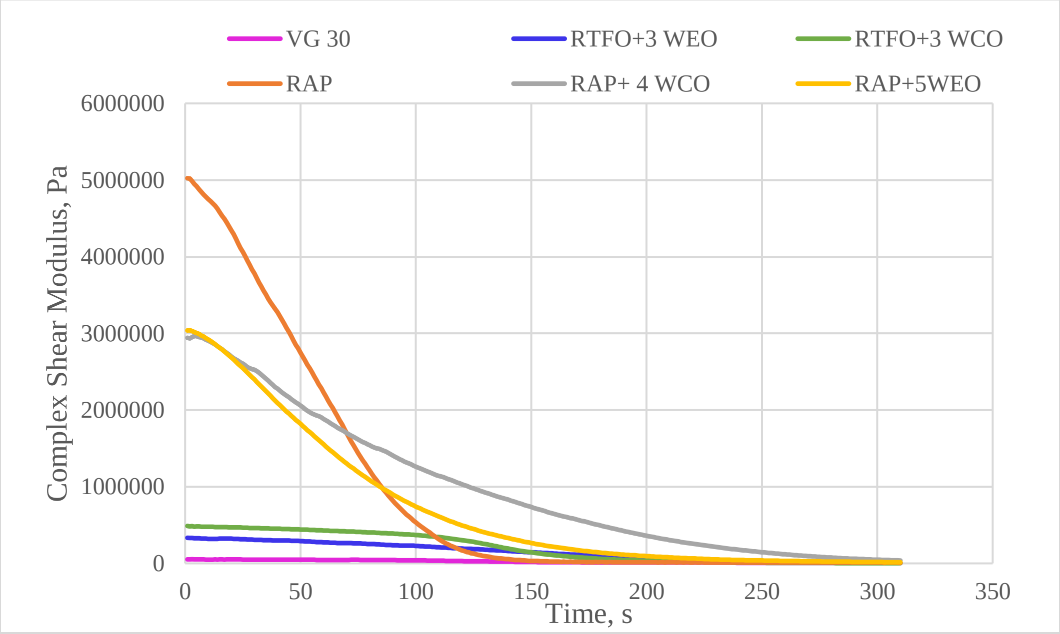

Figure 4.22: Variation in Complex Shear Modulus with Time at 40ºC

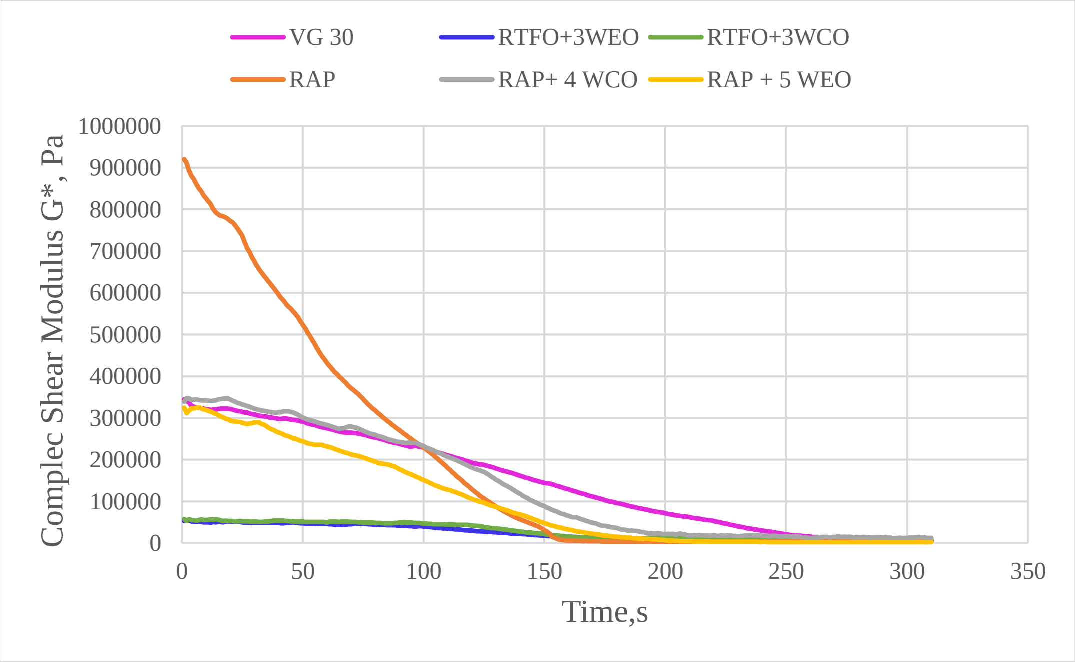

Figure 4.23: Variation in Complex Shear Modulus with Time at 60ºC

From Figure 4.23, it can be concluded that only VG 30 can withstand the increasing loading cycle and its stiffness reduced to zero only at 250 s, others attained zero stiffness around 150 s. Decrease in order of G* with time at 40ºC is as RAP < RAP+4 %WCO and RAP+5%WEO < RTFO+3

%WCO < RTFO+3% WEO < VG 30. At 60ºC G* value decreases and the decreasing order is as, RAP< RAP+4%WCO, RAP+5%WEO and VG 30 < RTFO+3%WCO and RTFO+ 3 %WEO respectively.

4.5.2.2 Variation in Phase Angle with Change in Time

Figure 4.24 and Figure 4.25 shows the variation in phase angle with loading time at 40ºC and 60ºC respectively. Analysing the variation in phase angle can help in understanding whether binder is in visco elastic region or not. From Figure 4.24 VG 30 and RAP attains purely viscous state from 200 seconds. RAP with rejuvenators never attains purely viscous state during the entire loading cycles. RTFO cum rejuvenated samples attains viscous state at 200 and 300 s. From Figure 4.25 all bituminous sample belong to visco-elastic state during the entire loading cycles. RAP binder and RAP +5% WEO shows fluctuation between zero to 90º at 200 and 300 s respectively, other samples attain purely viscous state at different stages of loading. At both temperatures VG30 and rejuvenated RTFO samples have comparatively higher phase angle than RAP and Rejuvenated RAP samples, hence relatively viscous in nature. Relatively less aged binder possesses higher maltene content with resins, hence found to be viscous in nature.

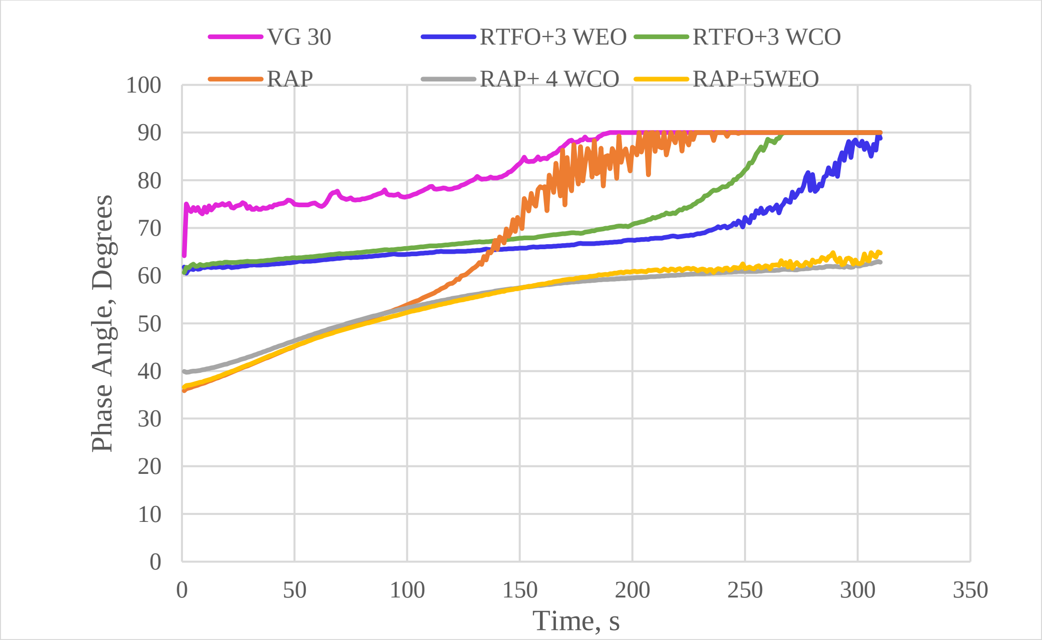

Figure 4.24: Variation in Phase Angle with Time at 40ºC

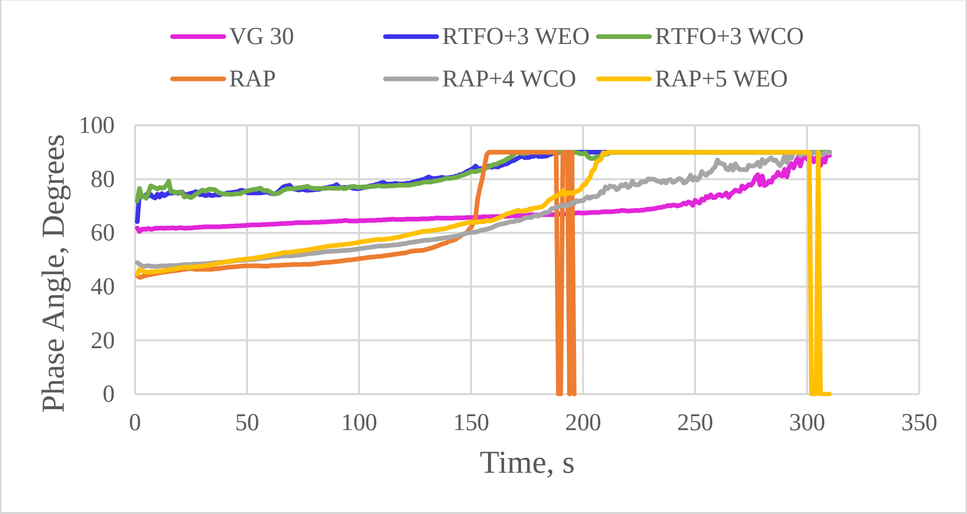

Figure 4.25: Variation in Phase Angle with Time at 60°C

4.5.2.3 Variation in Fatigue Parameter with Change in Time

Figure 4.26 and Figure 4.27 represents the variation in fatigue parameter with time at 40°C and 60°C respectively. Fatigue parameter is high for highly aged sample, here for RAP. As degree of aging reduces or with rejuvenation fatigue parameter reduces, which is acceptable. At 40°C fatigue parameter of all the sample are higher than that of VG 30. At 60°C fatigue parameter of rejuvenated RTFO samples becomes less than that of VG 30. Binder subjected to greater load cycles undergoes reduction in adhesion between binder and aggregates and increase in stiffness are the reasons behind.

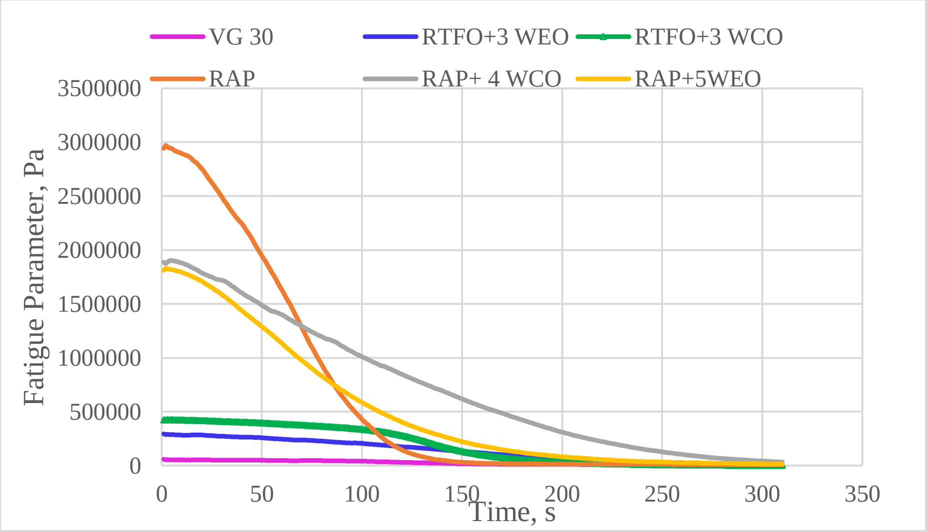

Figure 4.26: Variation in Fatigue Parameter with Time at 40°C

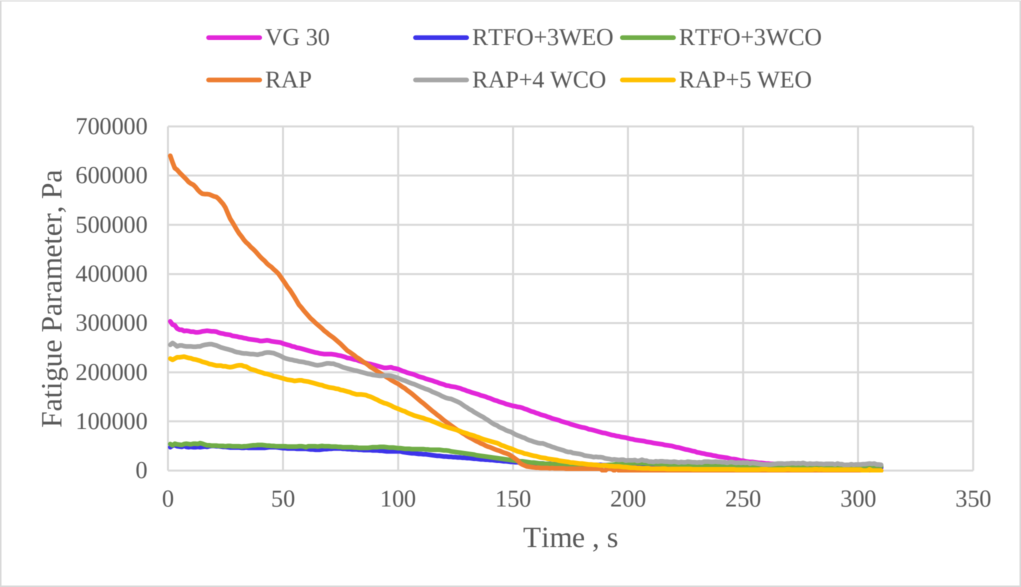

Figure 4.27: Variation in Fatigue Parameter with Time at 60ºC

4.5.2.4 Variation in Rutting Parameter with Change in Time

Figure 4.28 and Figure 4.29 shows the variation in rutting behaviour with loading cycles at 40ºC and 60ºC respectively. Rutting parameter also have same sort of variation with respect to time and at different temperatures. For the same time interval at different temperatures, rutting resistance decreases as temperature increases. At 40ºC all samples fall within VG 30 and at 60ºC, rutting parameter of rejuvenated RTFO sample is less than that of VG 30. Reduction in rutting resistance is due to increase in oil fraction due to rejuvenation and increase in temperature.

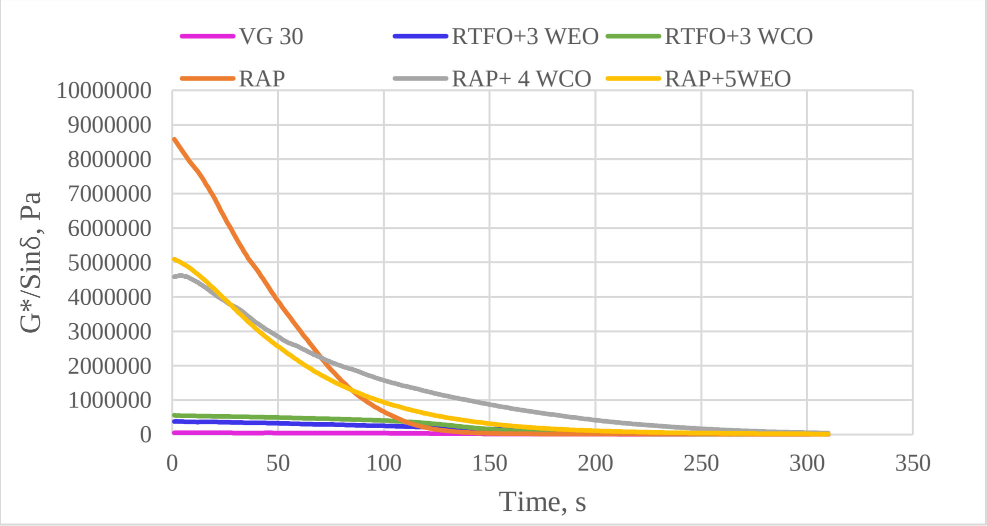

Figure 4.28: Variation in Rutting Parameter with Time at 40ºC

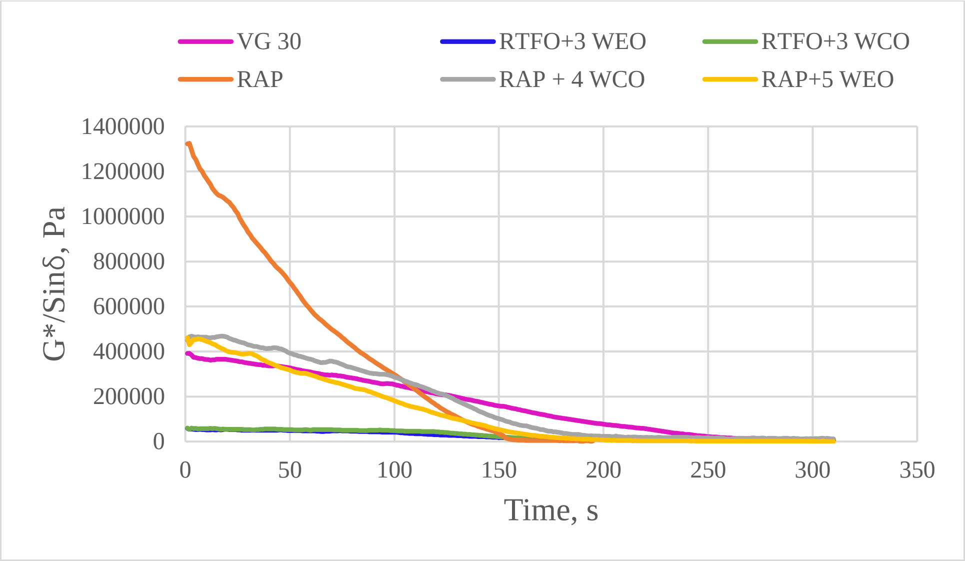

Figure 4.29: Variation in Rutting Parameter with Time at 60^{o}C

4.5.2.5 Variation in Shear Strain and Shear Stress in LAS Test at 60^{o}C and 40^{o}C

Figure 4.30 and Figure 4.31 represents the variation in shear stress with respect to shear strain. From Figure 4.30 certain inferences are made such that, RAP binder is having higher stress value and as rejuvenators are added, peak reduces. As peak reduces it shifts to the RHS side, hence strain corresponding to maximum stress varies.

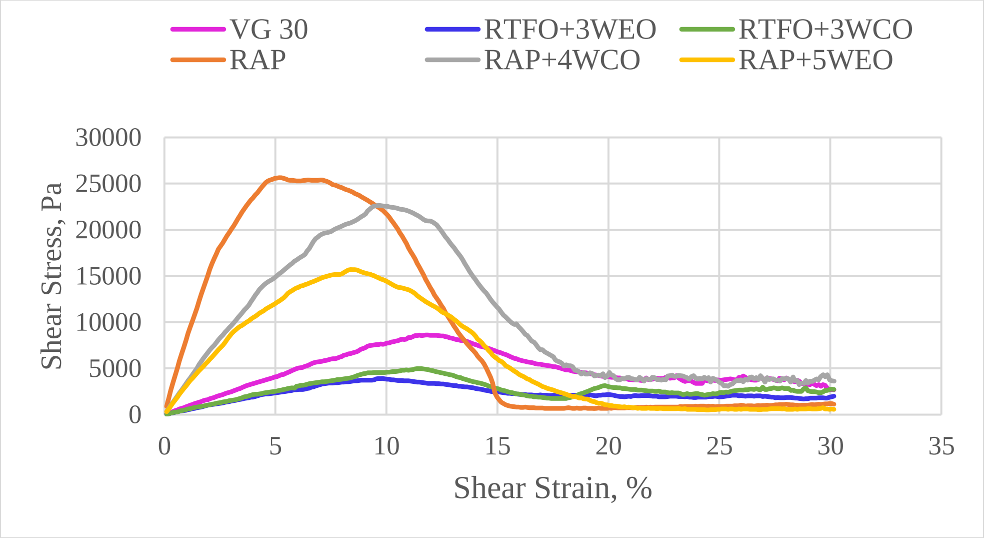

Figure 4.30: Variation in Shear Strain and Shear Stress in LAS Test at 60^{o}C

Rejuvenated samples of RAP are having peak stress value between RAP and unaged VG 30. Maximum shear stress value corresponding to RTFO aged- rejuvenated samples are less than that of VG 30. It is expected to have higher shear stress with relatively higher strain value, so that the material can withstand maximum stress till it undergoes maximum deformation. From Figure 4.31, pattern of variation in shear stress with shear strain is similar to that of variations at 60ºC. Maximum value of shear stress for RAP at 40ºC is around 5 times that at 60ºC. Shear stress of all the samples becomes constant at 20% for 60ºC and the constant is attained at 30% for 40ºC, except RAP +4% WCO. From Figure 4.30 and Figure 4.31, RAP + 4 %WCO can be considered as better rejuvenator since it can withstand maximum shear stress, here corresponding to 10% strain value.

4.5.2.6 Variation in Shear Strain and Shear Stress in LAS Test at 40ºC

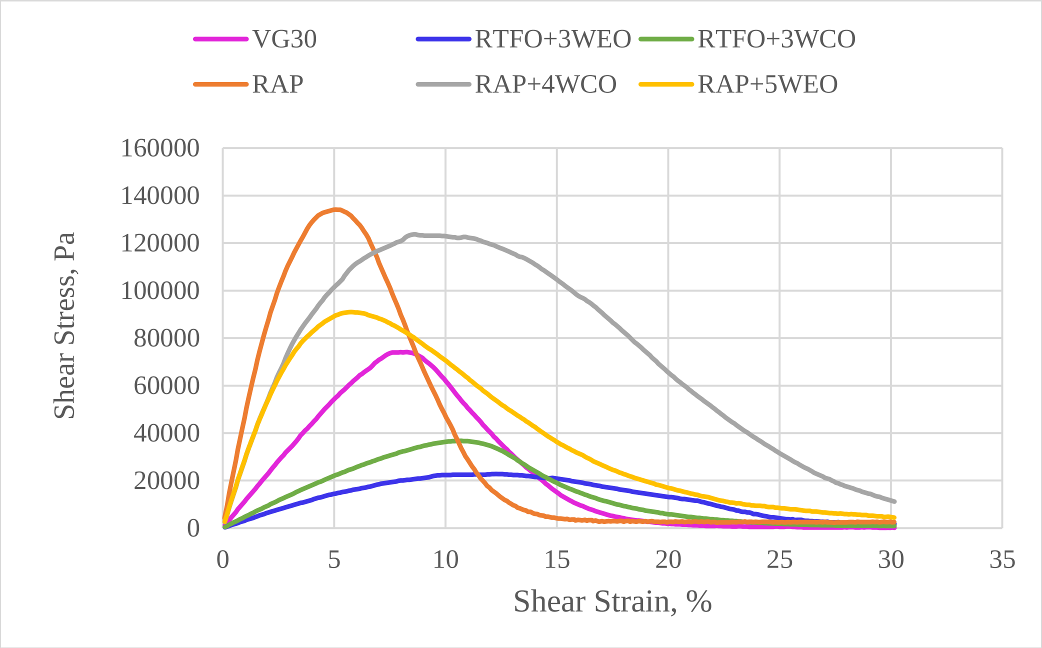

Figure 4.31: Variation in Shear Strain and Shear Stress in LAS Test at 40ºC

4.6 SUMMARY

Material testing procedure starts with physical property analysis to find the optimum dosage of rejuvenators. With the optimum dosage chemical and rheological properties are verified. From physical property analysis for RTFO aged sample 3% WEO and 3% WCO are found optimum; in case of RAP binder 5% WEO and 4% WCO are found optimum. In chemical analysis rejuvenation with WCO is found comparatively efficient in reducing the aging indices for rejuvenated RTFO samples and WEO for rejuvenated RAP samples. Rheological analysis with DSR shows that RAP binder with WCO and WEO rejuvenators are capable of bringing down the aged properties comparable to VG 30, but for RTFO aged samples with rejuvenation binder properties falls below unaged VG 30.

CHAPTER 5

CONCLUSIONS

5.1 GENERAL

Analysis of various properties of binder at different aging condition is analysed in different categories like physical, chemical and rheological properties. There are positive results obtained, where all such samples are compared with unaged VG 30. This study gave an insight about the aging of binder, factors influencing aging, methods to restore the binder properties, comparison between different rejuvenators and advanced technologies like RTFO aging, extraction and recovery of binder, FTIR and DSR. Following are the specific conclusions from the test results.

5.2 SPECIFIC CONCLUSIONS

- From physical properties there is considerable deterioration in binder properties due to RTFO aging and long-term in-service aging.
- WCO is found to be better than WEO in restoring physical properties such as decrease in softening point by 1.5°C, an increase in penetration by 1.25mm, a decrease in viscosity by 10 cP and 3% reduction in elastic recovery in comparison with 3% WEO.
- From chemical analysis, identical functional groups in VG 30 and rejuvenators showed that there are possibilities of blending of these two materials in an effective way.
- SI and CI values are found to be higher for RTFO aged because of shoot up in the degree of aging at high temperature. There is clear complimentary variation between aromatic and aliphatic compounds.
- 3% WCO is found effective compared to 3% WEO on RTFO aged binder to reduce the aging as per chemical analysis.
- 5% WEO and 4% WCO are found effective in reducing the aging of RAP binder but 5% WEO is found efficient as an optimum dosage in terms of chemical properties.
- From rheological property, complex shear modulus, rutting and fatigue criteria is found to be increasing with frequency and time at different rate but phase angle is having an inverse relation with time and frequency of loading. This is because of variation in stiffness and visco-elastic nature of bitumen due to change in temperature and rate of loading.

- As per LAS test the maximum stress is attained at 10% strain. At 40ºC, the maximum stress value is 120000 Pa and at 60ºC it is 25000 Pa. Comparatively maximum stress is attained at 40ºC corresponding to 10% strain which is considered as a better material property.
- Considering the variations between shear strain and shear stress, RAP +4% WCO is found effective.

5.3 APPLICATIONS OF WORK

This work is having greater relevance, since we are facing lack of construction materials, environmental degradation and greenhouse gas emission. Better way to eliminate this situation is to adopt sustainable development practices, where we can reduce, reuse and recycle the existing pavement materials. This particular study concentrates on reusing the flexible pavement material, RAP to reduce the need for virgin aggregates and binder which are non-renewable in nature. This can reduce the exploitation of natural resources and problems related to disposal of demolished or milled materials.

Considering rejuvenators, the study concentrates on waste engine oil and waste cooking oil; both are easily available in Kerala and cost effective. In restoring physical properties WCO is found to be effective for RTFO aged binder; both WEO and WCO can be suggested for RAP binder at optimum dosages. In case of chemical properties, for RAP binder WEO is found effective and WCO for RTFO aged binder. WCO at optimum dosage is found to be effective in rheological property by withstanding maximum stress corresponding to strain.

5.4 FUTURE SCOPE OF WORK

There is various scope for future work to develop meaningful insight regarding the topic. Some of them are comparison of degree of aging in PAV aged binder with RTFO aged and RAP binder. Morphological analysis of specimens can be done to evaluate the micro level surface character which is lacking in this study. Light reflecting or absorbing property of binder with rejuvenators can be studied to quantify the urban heat island effects; moisture susceptibility and skid resistance of rejuvenated binder need to be studied to quantify the durability and functional performance of recycled binder. Quantifying the sustainable benefits of rejuvenation in terms of materials saved, cost reduction and environmental conservation are also important.

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