

**PERFORMANCE ANALYSIS OF WASTE COOKING OIL GRANULATE
MODIFIED BITUMEN AND ASPHALT MIXTURES**

By

ZAFREEN ELAHI

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia,
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DEDICATION

This thesis is specially dedicated to:

My beloved parents

&

My Husband



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment
of the requirement for the degree of Doctor of Philosophy

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The global demand for non-renewable resources like bitumen in flexible pavement construction is a significant concern, prompting researchers to seek alternative solutions like bio-modifiers. Waste cooking oil (WCO) has shown promise in enhancing bitumen and asphalt properties, yet its use is limited due to its oily nature affecting high-temperature bitumen performance. Therefore, a pre-modification of the WCO was proposed using the Styrene Butadiene Styrene (SBS) to change its phase from liquid to a rubbery solid state. Conversely, a significant difference in molecular weight in SBS modifiers and bitumen is the reason for their limited thermal compatibility with each other. The introduction of SBS directly into the bitumen results in significant segregation issues and high energy consumption to produce modified bitumen. Whereas its utilisation in conjunction with the WCO improves overall performance and mitigates these challenges. This study aims to explore the impact of modified waste cooking oil on bitumen and asphalt mixture performance.

The characterization of the raw materials i.e., bitumen, WCO, and aggregates was followed in the study's first objective. The preliminary raw materials assessment suggests that the results are within the specification and suitable for further testing and analysis. The filtered WCO was modified by blending the SBS: WCO at 20:80, 30:70, 40:60, 45:55 and 50:50. The Modified WCO Granulates (MWCOG) were blended with bitumen by weight at various ratios with concentrations of 5%, 10%, 15%, 20%, and 25%. These blended modified bitumens underwent testing for rotational viscosity and rutting parameters and were analysed for their suitability. Hence, the key finding is that the optimum ratio suitability for the bitumen modification is MWCOG-45:55 and MWCOG-50:50. The second objective of the study was to evaluate the effectiveness of the MWCOG-45:55 and MWCOG-50:50 on bitumen's rheological, physical, morphological and chemical properties. Based on the viscosity results, the increasing content of the MWCOG has increased the stiffening of the base bitumen. Adding 5–25 wt.% of MWCOG-45:55 improves the viscosities in the range of 513–3512.2 cp at 135 °C. However, the MWCOG-50:50 displayed a slightly higher viscosity with values of 562.1–2988.2 cp. It is noteworthy that the performance grading (PG) of the base bitumen is improved from PG64 to PG76 whilst adding the 10% of MWCOG-50:50. Moreover, the Black space diagram curves have shifted towards the lower phase angle (δ) with smooth curves indicating the improvement in the performance of the modified bitumens, and 45:55-25% and 50:50-25% curves are not desirable, indicating the marginal change in δ at higher and lower temperatures. The master curve of 45:55-15% has higher stiffness at a lower frequency than other bitumen curves and is less stiff at a higher frequency. The microstructure analysis showed that there is no such difference in homogeneity between 45:55-10% and 50:50-10% which further clarifies the principle of the rapid dissolution of SBS particles in WCO.

The third objective's findings for the selective Marshall mix design are derived from the process of elimination established in the second objective, which assesses the optimum bitumen content (OBC). The results suggested that the increasing content of the MWCOG for the bitumen modification eventually decreases the OBC of the asphalt mixtures. The control mixture OBC is 5.04% which is slightly higher than 45:55-10% and 50:50-10% with 4.92% and 4.89% respectively. The study's fourth objective evaluates the mechanical characteristics of the opted asphalt mixtures. There is no notable enhancement in the overall stiffness of asphalt mixtures. However, the 45:55-5% and 50:50-5% have demonstrated an improvement of 13.5% and 0.33% compared to the control mixture respectively. Additionally, the permanent deformation evaluation showed a significant decrease in the cumulative strain of modified asphalt mixtures. The 45:55-5% and 50:50-5% have a strain value of 0.46% and 0.54% respectively which is lower than the 0.63% of the control mixtures. However, the control mixture has demonstrated a lower creep modulus of 239 Mpa compared to the 45:55-5% and 45:55-10% with values of 323 Mpa and 277 Mpa respectively. The integration of the mixture test showed an average loss of 2.50% of the control specimens which is higher among all the modified mixtures. However, the MWCOG-45:55 demonstrated an overall lower average loss compared to the MWCOG-50:50. Thus, the study outcomes suggested that the modified WCO with a concentration of up to 10% has a significant impact on the properties of the bitumen and modified asphalt mixtures and possibly be an economical and sustainable modifier in pavement construction.

Keywords: Waste Cooking Oil, Viscosity, Rheological Properties, Bitumen, Rutting

SDG: Goal 9: Industry, Innovation and Infrastructure, Goal 11: Sustainable Cities and Communities.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah

**ANALISIS PRESTASI CAMPURAN BITUMEN DAN ASFALT TERUBAH
SUAI DENGAN GRANULAT MINYAK MASAK TERPAKAI**

Oleh

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Permintaan global untuk sumber tidak boleh diperbaharui seperti penggunaan bitumen dalam pembinaan turapan fleksibel adalah salah satu kebimbangan yang mendorong penyelidik mencari penyelesaian alternatif seperti pengubah bio. Minyak masak terpakai (WCO) telah menunjukkan potensi dalam meningkatkan kualiti bitumen dan asfalt, namun penggunaannya terhad disebabkan sifatnya yang mengganggu prestasi bitumen pada suhu tinggi. Oleh itu, pra-pengubahsuaian WCO telah dicadangkan dengan menggunakan Styrene Butadiene Styrene (SBS) untuk menukar fasa WCO daripada cecair kepada keadaan pepejal seperti getah. Perbezaan ketara dalam berat molekul antara pengubah SBS dan bitumen adalah sebab utama untuk keserasian terma antara keduanya. Pengenalan SBS secara langsung ke dalam bitumen menyebabkan isu pengasingan yang ketara dan penggunaan tenaga yang tinggi untuk menghasilkan bitumen yang diubah suai. Namun begitu, penggunaannya bersama dengan WCO meningkatkan prestasi bitumen secara keseluruhan dan mengurangkan cabaran-cabaran ini. Kajian ini bertujuan untuk meneroka kesan minyak masak terpakai yang telah diubahsuai terhadap prestasi bitumen dan campuran asfalt.

Pencirian bahan untuk bitumen, WCO, dan agregat telah diikuti dalam objektif pertama kajian ini. Penilaian bahan mentah menunjukkan bahawa ciri-ciri bahan mentah ini adalah dalam spesifikasi dan sesuai digunakan untuk ujian serta analisis selanjutnya. WCO yang ditapis diubah suai dengan mencampurkan SBS pada nisbah 20:80, 30:70, 40:60, 45:55 dan 50:50. Granul WCO yang telah diubah suai (MWCOG) dicampur dengan bitumen mengikut berat pada nisbah yang berbeza dengan kepekatan 5%, 10%, 15%, 20%, dan 25%. Bitumen ubah suai ini diuji untuk kelikatan putaran dan parameter mengarut serta dianalisis untuk kesesuaiannya. Oleh itu, penemuan utama menunjukkan kesesuaian nisbah optimum untuk pengubahsuaian bitumen ialah MWCOG-45:55 dan MWCOG-50:50. Objektif kedua kajian adalah menilai sifat reologi, fizikal, morfologi, dan kimia untuk MWCOG-45:55 dan MWCOG-50:50. Berdasarkan keputusan kelikatan, peningkatan kandungan MWCOG telah meningkatkan pengerasan bitumen asas. Penambahan 5 hingga 25 wt.% MWCOG-45:55 meningkatkan kelikatan dalam julat 513 hingga 3512.2 cp pada suhu 135 °C. Walau bagaimanapun, MWCOG-50:50 menunjukkan kelikatan yang lebih tinggi dengan nilai 562.1 hingga 2988.2 cp. Penarafan prestasi (PG) bitumen asas dipertingkatkan daripada PG64 kepada PG76 apabila ditambah dengan 10% MWCOG-50:50. Selain itu, lengkung gambarajah ruang Hitam telah beralih ke arah sudut fasa (δ) yang lebih rendah dengan lengkung licin menunjukkan peningkatan dalam prestasi bitumen yang diubah suai, manakala lengkung 45:55-25% dan 50:50-25% menunjukkan perubahan marginal dalam δ pada suhu lebih tinggi dan lebih rendah. Lengkung induk 45:55-15% mempunyai ketegaran yang lebih tinggi pada frekuensi yang lebih rendah berbanding lengkung bitumen lain dan kurang tegar pada frekuensi yang lebih tinggi. Analisis mikrostruktur menunjukkan tiada perbezaan yang ketara dalam homogeniti antara 45:55-10% dan 50:50-10% yang menjelaskan prinsip pelarutan cepat zarah SBS dalam WCO.

Penemuan objektif ketiga adalah untuk reka bentuk campuran Marshall terpilih diperoleh daripada proses penyingkiran yang ditetapkan dalam objektif kedua, yang menilai kandungan bitumen optimum (OBC). Keputusan tersebut menunjukkan bahawa peningkatan kandungan MWCOG untuk pengubahsuaian bitumen secara beransur-ansur mengurangkan OBC campuran asphalt. Campuran kawalan OBC ialah 5.04%, iaitu lebih tinggi sedikit daripada 45:55-10% dan 50:50-10% dengan masing-masing 4.92% dan 4.89% . Objektif keempat kajian menilai ciri mekanikal campuran asphalt yang dipilih. Tiada peningkatan ketara dalam ketegaran keseluruhan campuran asphalt. 45:55-5% dan 50:50-5% mempunyai nilai ketegangan masing-masing 0.46% dan 0.54% yang lebih rendah daripada 0.63% campuran kawalan. Walau bagaimanapun, campuran kawalan telah menunjukkan modulus rayapan yang lebih rendah sebanyak 239 Mpa berbanding 45:55-5% dan 45:55-10% dengan nilai masing-masing sebanyak 323 Mpa dan 277 Mpa. Ujian pengintegrasian campuran menunjukkan purata kehilangan yang sebanyak 2.50% pada spesimen kawalan yang lebih tinggi di antara semua campuran yang diubah suai. Namun begitu, MWCOG-45:55 menunjukkan purata kehilangan keseluruhan yang lebih rendah berbanding MWCOG-50:50. Walau bagaimanapun, 45:55-5% dan 50:50-5% menunjukkan peningkatan sebanyak 13.5% dan 0.33% berbanding campuran kawalan. Selain itu, penilaian ubah bentuk kekal menunjukkan penurunan yang ketara dalam regangan kumulatif campuran asphalt yang diubah suai. Oleh itu, hasil kajian ini mencadangkan bahawa WCO yang diubah suai dengan kepekatan sehingga 10% memberi kesan yang ketara ke atas sifat bitumen dan campuran asphalt yang diubah suai, dan berpotensi menjadi pengubah yang ekonomi dan mampan dalam pembinaan turapan.

Kata Kunci: Minyak Masak Terpakai, Kelikatan, Sifat Reologi, Bitumen, Keruntuhan

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TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iv
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	x
LIST OF TABLES	xv
LIST OF FIGURES	xix
LIST OF ABBREVIATIONS	xxiv
 CHAPTER	
 1 INTRODUCTION	 1
1.1 General background	1
1.2 Problem Statement	5
1.3 Objectives of the study	7
1.4 Scope and limitations of the study	7
1.5 Novelty and contribution	10
1.6 Thesis outlines	10
 2 LITERATURE REVIEW	 12
2.1 Introduction	12
2.2 Waste cooking oil	12
2.2.1 Production of waste cooking oil	14
2.2.2 Physical and chemical properties of WCO	15
2.2.3 Free fatty acid (FFA) in WCO	17
2.3 Application of WCO as bio-bitumen in pavement industry	19
2.3.1 Effect of WCO on conventional properties of bitumen	22
2.3.2 Effect of WCO on rheological properties of bitumen	25
2.3.3 Effect of WCO with additional additives on conventional properties	29
2.3.4 Effect of WCO with additional additives on rheological properties	33
2.3.5 The impact of WCO on the performance of asphalt mixtures	37
2.3.6 Fourier transform infrared spectroscopy of WCO modified bitumens	41
2.4 Theoretical framework of the study	42
2.5 Summary	47
 3 METHODOLOGY	 48
3.1 Introduction	48
3.2 Characterisation of Materials (Objective 1)	50
3.2.1 Properties of bitumen	50
3.2.2 Properties of aggregates	51

3.2.3	Properties of Styrene Butadiene Styrene	52
3.3	Properties of waste cooking oil	52
3.3.1	Structure and surface morphology of materials	53
3.3.2	Elemental analysis and chemical composition	54
3.3.3	Pre-processing and modification of WCO	54
3.4	Preparation process of modified bitumens (Blending)	56
3.5	Identification of optimal MWCOG ratio	58
3.6	Characterization of WCO modified bitumen (Objective 2)	59
3.6.1	Ageing of base and modified bitumen	59
3.7	Rotational viscosity	62
3.8	Dynamic rheological properties of bitumen	64
3.8.1	DSR testing procedure	64
3.8.2	Temperature sweep	67
3.8.3	Frequency sweep	68
3.9	Separation index of modified bitumen	71
3.10	FTIR analysis of bitumen	72
3.11	Process of elimination for blend selection	73
3.12	Marshall mix design (Objective 3)	73
3.12.1	Aggregate gradation	73
3.12.2	Marshall cylindrical specimens preparation	74
3.12.3	Determination of asphalt mixture's volumetric properties	76
3.12.4	Marshall Stability and Flow	79
3.12.5	Resilient modulus (M_R)	80
3.12.6	Selection of optimum bitumen content (OBC)	82
3.13	Performance analysis of mixtures (Objective 04)	82
3.13.1	Dynamic creep/rutting test	82
3.13.2	Cantabro test	86
3.14	Statistical analysis	88
3.15	Summary	90
4	RESULTS AND DISCUSSION	91
4.1	Materials characterisation (Objective-01)	91
4.1.1	Properties of Bitumen	92
4.1.2	Properties of aggregates	93
4.1.3	Properties of waste cooking oil and Styrene butadiene styrene	94
4.2	Properties of modified waste cooking oil granulates	95
4.2.1	Physical properties modified WCO granulates	95
4.2.2	Surface morphology of MWCOG	96
4.2.3	Energy-dispersive X-ray (EDX) of MWOGs	98
4.3	Identification of optimal MWCOG ratio	101
4.3.1	Modified WCO granulates-20:80 and 50:50	101
4.4	Summary of identification of optimal ratio of MWCO granulates	112
4.5	Modified WCO bitumen properties at the optimal ratio of MWCOG (Objective 2)	115
4.5.1	Rotational viscosity of MWCOG modified bitumen	115
4.5.2	Ageing indices of modified bitumens	123

4.5.3	Dynamic rheological properties of MWCOG modified bitumens	125
4.5.4	Temperature sweeps of modified bitumens	126
4.5.5	Frequency sweep of MWCOG modified bitumens	141
4.6	Storage stability test of modified bitumen	164
4.7	Morphological analysis of MWCOG and modified bitumen	167
4.8	Energy-dispersive X-ray (EDX) and mapping of modified bitumens	169
4.9	FTIR analysis of selected blends	174
4.10	Process of elimination for blends	175
4.11	Summarised results of Objective 2	176
4.12	Hot mix asphalt mix design (Objective 3)	179
4.12.1	Aggregate gradation	179
4.12.2	Marshall mix design and specimen preparation	181
4.12.3	Volumetric properties of all mixtures	181
4.12.4	Selection of optimum bitumen content	188
4.13	Summarised results of Objective 3	190
4.14	Mechanical performance of asphalt mixtures (Objective 4)	191
4.14.1	Marshall stability and flow	192
4.14.2	Resilient modulus (M_R)	196
4.14.3	Rutting/Dynamic creep	201
4.14.4	Cantrabro test	208
4.15	Two-way ANOVA analysis	211
4.15.1	MWCOGs bitumen	212
4.15.2	MWCOGs asphalt mixtures	217
4.16	Summary	222
5	CONCLUSION AND RECOMMENDATIONS	223
5.1	Introduction	223
5.2	Conclusion	223
5.3	Recommendations for further research	228
	REFERENCES	230
	APPENDICES	242
	BIODATA OF STUDENT	272
	LIST OF PUBLICATIONS	273

LIST OF TABLES

Table	Page
2.1 Physical properties of WCO	15
2.2 Variation in the chemical composition of oil after the frying process	16
2.3 Hydrolysis of triglycerides	19
2.4 Classifications of bio-bitumens	19
2.5 Mixing variables for WCO modified binder	20
2.6 Summary of the reviewed literature on the use of WCO and additives at various concentrations	21
3.1 Bitumen tests, standards and specifications	51
3.2 Aggregates standards, specifications, and tests	51
3.3 Modification proportion of SBS and WCO	55
3.4 Studied bitumen description	58
3.5 AC14 HMA gradation specifications	74
3.6 Resilient modulus test setup parameters	81
3.7 Dynamic creep test setup parameters	84
4.1 Empirical test results of base bitumen	92
4.2 Granite aggregate test results	93
4.3 Waste cooking oil and SBS properties results	95
4.4 Basic properties of modified WCO granulates	96
4.5 Elemental composition of MWCOG-45:55	99
4.6 Elemental composition of MWCOG-50:50	100
4.7 Rotational viscosity results of modified bitumen at 20:80	102
4.8 Rotational viscosity results of modified bitumen at 50:50	103
4.9 Mixing and compaction temperatures of 20:80 modified blends	106
4.10 Mixing and compaction temperatures of 50:50 modified blends	107

4.11	Shift factors and slope (%) of 20:80 modified bitumen	109
4.12	Shift factors and slope (%) of 50:50 modified bitumen	109
4.13	Rutting parameter of 20:80 at varying temperatures	110
4.14	Rutting parameter of 50:50 at varying temperatures	110
4.15	Summarised results of modified bitumen blends at various modified WCO ratios	114
4.16	Rotational viscosity of unaged and aged 45:55 modified bitumens	116
4.17	Rotational viscosity of unaged and aged 50:50 modified bitumens	116
4.18	Rotational viscosity rate of increase of modified bitumens 45:55	119
4.19	Rotational viscosity rate of increase of modified bitumens 50:50	119
4.20	Mixing and compaction temperatures of modified bitumens	120
4.21	Slope of 45:55 and 50:50 modified bitumen	123
4.22	Viscosity ageing indices of modified bitumens	124
4.23	Temperature sweep results of unaged base and modified bitumen at varying temperatures	127
4.24	Temperature sweep results of aged base and modified bitumen at varying temperatures	131
4.25	Rutting parameter of all blends at 64 °C and PG grading	133
4.26	Rutting rate of increase of unaged and aged blends at 64 °C	138
4.27	Temperature sweep results of PAV aged base and modified bitumen at varying intermediate temperatures	139
4.28	Fatigue parameters of base and modified bitumens at 16 °C	141
4.29	Complex modulus (kPa) results of 45:55 and 50:50 modified bitumen at 0.10 Hz and 13 Hz	143
4.30	Phase angle results of 45:55 and 50:50 modified bitumen at 0.10 Hz and 13 Hz	143
4.31	Sigmoidal models-WLF equation parameters and coefficients for unaged bitumens	153
4.32	Predicting equation of unaged MWCOG modified bitumens	154
4.33	Sigmoidal models-WLF equation parameters and coefficients for RTFO aged bitumens	156

4.34	Predicting equation of RTFO aged MWCOG modified bitumens	158
4.35	Angle between G' and G'' of 45:55 and 50:50 modified bitumens	161
4.36	Complex modulus at 64 °C of MWCOG-45:55 and MWCOG-50:50 modified bitumens after storage stability test	164
4.37	Elemental composition of 45:55 modified bitumen	171
4.38	Elemental composition of 50:50 modified bitumen	173
4.39	Summarised results of MWCOG-45:55 and MWCOG-50:50 modified bitumen	178
4.40	Specification of AC14 HMA aggregate gradation	180
4.41	Volumetric properties of control mixture	184
4.42	Marshall mix design results of control mixture	186
4.43	Summarised volumetric properties of seven mixture designs	186
4.44	Optimum bitumen content of seven asphalt mixtures	189
4.45	Marshall stability results of MWCOG asphalt mixtures	192
4.46	Marshall flow results of MWCOG asphalt mixtures	192
4.47	Marshall stability and flow results of asphalt mixtures	196
4.48	Resilient modulus of asphalt mixture at 25 °C	197
4.49	Resilient modulus of asphalt mixture at 40 °C	197
4.50	Percentage differences in resilient modulus of 45:55 and 50:50 mixtures	200
4.51	Dynamic creep test results of five asphalt mixtures	201
4.52	Slope (%) of all asphalt mixtures at zone-I and zone-II	203
4.53	Creep modulus and creep rate of asphalt mixtures	205
4.54	Cantrabro test results of MWCOG asphalt mixtures.	208
4.55	Two way ANOVA rotational viscosity	212
4.56	Two way ANOVA complex modulus	213
4.57	Post hoc multiple comparisons of rotational viscosity	213
4.58	Post hoc multiple comparisons of complex modulus	216

4.59	Two way ANOVA Marshall stability	218
4.60	Two way ANOVA resilient modulus	218
4.61	Post hoc multiple comparisons of Marshall stability	219
4.62	Post hoc multiple comparisons of resilient modulus	219



LIST OF FIGURES

Figure	Page
1.1 Global vegetable oil consumption Worldwide by oil type	3
2.1 Waste cooking oil	14
2.2 Physical and chemical changes in oil during deep-frying	17
2.3 Chemical composition of WCO	18
2.4 Effect of WCO content on bitumen: (a) Penetration, (b) Rotational viscosity	23
2.5 Rutting parameters of asphalt binders at various content of WCO	26
2.6 Failure temperatures of untreated and treated modified asphalt binders	27
2.7 Effect of WCO and HDPE contents on asphalt binder: (a) softening, (b) Penetration resistance	31
2.8 Effect of WCO and GTR content on the rotational viscosity at 135 °C	32
2.9 Predicted fatigue life of WCO and GTR modified bitumens	35
2.10 Creep stiffness and m-value of WCO and SBS/EVA modified bitumen	37
2.11 Marshal stability of asphalt mixtures	38
2.12 Dynamic stability of different HMA	39
2.13 FTIR spectra of untreated and chemically treated WCO	42
2.14 Illustration of SBS (a) linear SBS with high butadiene (b) with high styrene (c) radial SBS molecule	44
2.15 Schematic illustration of SBS influence on bitumen	45
3.1 Flow chart of the study	49
3.2 Styrene Butadiene Styrene (SBS)	52
3.3 Morphological analysis of materials	53
3.4 Steps involved in modification of WCO	56
3.5 Blending process of MWCOG-bitumen	57

3.6	Short-term ageing of base and modified bitumen using RTFO	60
3.7	PAV and vacuum chamber for bitumen long-term ageing	61
3.8	Steps involved in PAV test	62
3.9	Rotational viscometer	63
3.10	Dynamic shear rheometer	65
3.11	Steps involved in the preparation of DSR sample	66
3.12	Process of storage stability test	72
3.13	Cylindrical compacted specimens	75
3.14	Marshall stability setup	80
3.15	Test set up resilient modulus	81
3.16	Trimmed Marshall specimen for dynamic creep test	84
3.17	Rutting test setup	86
3.18	Cantabro test specimens: (a) before test (b) after test	88
4.1	FESEM images of modified waste cooking oil: (a) 45:55 (b) 50:50	97
4.2	EDX spectra of modified WCO ratio 45:55	99
4.3	EDX spectra of modified WCO ratio 50:50	100
4.4	Viscosity results of 20:80 modified bitumen at varying temperatures	104
4.5	Viscosity results of 50:50 modified bitumen at varying temperatures	104
4.6	Viscosity slope of 20:80 and 50:50 modified bitumen at (a) zone-I (b) zone-II	105
4.7	Viscosity-temperature relationship of 20:80 blends	108
4.8	Viscosity-temperature relationship of 50:50 blends	108
4.9	Temperature effect on rutting parameter of 20:80 modified blends	111
4.10	Temperature effect on rutting parameter of 50:50 modified blends	112
4.11	Rotational viscosity of unaged and aged modified bitumens: (a) 45:55 (b) 50:50	118
4.12	Mixing and compaction temperature of 45:50 modified bitumens	121
4.13	Mixing and compaction temperature of 50:50 modified bitumens	121

4.14	Effect of modified WCO on mixing and compaction temperatures	122
4.15	Viscosity ageing indices of modified bitumen at (a):135 °C (b):165°C	125
4.16	Isochronal plots of complex modulus and phase angle of unaged WCO modified bitumen: (a) 45:55 (b) 50:50	129
4.17	Isochronal plots of complex modulus and phase angle of aged WCO modified bitumen; (a) 45:55 (b) 50:50	132
4.18	Temperature effect on rutting parameter ($G^*/\sin \delta$) of 45:55 and 50:50 unaged blends	134
4.19	Effect of MWCOG on the failure temperatures of unaged modified bitumens	135
4.20	Effect of MWCOG on a rutting parameter of unaged modified bitumens at 64 °C	136
4.21	Temperature effect on rutting parameter ($G^*/\sin \delta$) of 45:55 and 50:50 aged blends	137
4.22	Effect of MWCOG on rutting parameter of aged modified bitumens at 64 °C	138
4.23	Temperature effect on fatigue parameter ($G^*.\sin \delta$) of MWCOG	140
4.24	Effect of WCOBs on fatigue parameter of modified bitumens at 16 °C	141
4.25	Frequency plots of unaged 45:55 modified bitumens at (a) 35 °C, (b) 45 °C, (c) 55 °C, (d) 65 °C, (e) 75 °C, (f) 85 °C	147
4.26	Black space diagram of unaged MWCOG-45:55 modified blends	149
4.27	Black space diagram of RTFO aged MWCOG-45:55 modified blends	149
4.28	Black space diagram of unaged MWCOG-50:50 modified blends	151
4.29	Black space diagram of aged MWCOG-50:50 modified blends	151
4.30	Complex modulus master curves of unaged MWCOGa-45:55 at a reference temperature of 65 °C	154
4.31	Complex modulus master curves of unaged MWCOGa-50:50 at a reference temperature of 65 °C	155
4.32	Complex modulus master curves of aged MWCOGa-45:55 at a reference temperature of 65 °C	157

4.33	Complex modulus master curves of unaged MWCOGa-50:50 at a reference temperature of 65 °C	157
4.34	Cole-Cole plot of unaged 45:55	159
4.35	Cole-Cole plot of RTFO aged 45:55	160
4.36	Angle between G' and G'' of 45:55 and 50:50 unaged modified bitumens	161
4.37	Angle between G' and G'' of 45:55 and 50:50 RTFO aged modified bitumens	162
4.38	Cole-Cole plot of unaged 50:50	163
4.39	Cole-Cole plot of RTFO aged 50:50	163
4.40	Storage stability results of MWCOG-45:55	165
4.41	Storage stability results of MWCOG-50:50	166
4.42	Comparative assessment of 45:55 and 50:50 modified bitumen separation indices	166
4.43	SEM images of MWCOG (a) 45:55 (b) 50:50	168
4.44	FESEM images of base and MWCOG modified bitumen: (a) Base bitumen, (b) 45-55-10%, (c) 50:50-10%	169
4.45	FESEM mapping images and EDX spectra of modified bitumen 45:55 (a),(b),(c) Mapping images (d) EDX spectra.	171
4.46	FESEM mapping images and EDX spectra of modified bitumen 50:50 (a),(b),(c) Mapping images (d) EDX spectra	173
4.47	FTIR spectra of MWCOG-45:55 and MWCOG-50:50	175
4.48	Aggregates particle size distribution curves	180
4.49	Optimum bitumen content determination plots for control mixture	185
4.50	Volumetric properties of seven mixtures at OBC	187
4.51	Optimum bitumen content of seven asphalt mixtures	190
4.52	OBC rate of decrease of 45:55 and 50:50 mixtures	190
4.53	Marshal stability results of MWCOG modified mixtures: (a) 45:55 (b) 50:50	194
4.54	Marshal flow results of MWCOG modified mixtures: (a) 45:55 (b) 50:50	196

4.55	Resilient modulus results of MWCOG modified mixtures at 25 °C: (a) 45:55 (b) 50:50	198
4.56	Resilient modulus results of MWCOG modified mixtures at 40 °C: (a) 45:55 (b) 50:50	200
4.57	Cumulative strain (%) of modified asphalt mixture: (a) 45:55 (b) and 50:50 at 3600 cycles	202
4.58	Total permanent strain (%) versus number of cycles of 45:55 asphalt mixtures	204
4.59	Total permanent strain (%) versus number of cycles of 50:50 asphalt mixtures	204
4.60	Comparative assessment of 45:55 and 50:50 creep modulus	206
4.61	Comparative assessment of 45:55 and 50:50 creep rate	207
4.62	Cantrabro test results of asphalt mixtures 45:55	210
4.63	Cantrabro test results of asphalt mixtures 50:50	210
4.64	Comparative assessment of average loss of 45:55 and 50:50 mixtures	211
4.65	Estimated means of rotational viscosity at varying WCO%	217
4.66	Estimated means of complex modulus at varying WCO%	217
4.67	Estimated means of Marshall stability at varying WCO%	221
4.68	Estimated means of resilient modulus at varying WCO%	221

LIST OF ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
AC	Asphalt concrete
ASTM	American Society of Testing and Materials
CR	Crumb Rubber
DSR	Dynamic Shear Rheometer
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
FST	Frequency Sweep Test
FTIR	Fourier Transform Infrared Spectroscopy
HMA	Hot Mix Asphalt
ITS	Indirect Tensile Strength
JKR	Jabatan Kerja Raya
LVDTs	Linear Variable Differential Transducer
LVE	Linear Visco Elastic
MATTA	Material Testing Apparatus
MEPDG	Mechanistic-empirical Pavement Design Guide
MMT	Million Metric Ton
MWCOGs	Modified waste cooking oil granulates
NCHRP	National Cooperative Highway Research Program
OBC	Optimum Bitumen Content
PAV	Pressure Ageing vessel
PMBs	Polymer Modified Bitumen's
RLAT	Repeated Load Axial Test
RM	Resilient Modulus

RTFO	Rolling Thin Film Oven
SBS	Styrene-Butadiene-Styrene
SHRP	Strategic Highway Research Program
TMD	Theoretical Maximum density
TSR	Tensile Strength Ratio
TST	Temperature Sweep Test
TTSP	Time Temperature Superposition Principle
UTM	Universal Testing Machine
VAI	Viscosity Ageing Index
VFB	Voids Filled with Bitumen
VMA	Voids in Mineral Aggregates
VTM	Voids in Total Mix
WCO	Waste Cooking Oil
WLF	Williams, Landel, and Ferry's
WMA	Warm Mix Asphalt

CHAPTER 1

INTRODUCTION

1.1 General background

Over the last few decades, the fast growth of cities and the increasing number of automobiles have increased the demand for road pavement construction and maintenance (Fini et al., 2012). Around 95% of the world's roads are made of flexible pavement, and bitumen serves as a conventional material for pavement construction. Bitumen is a byproduct of crude oil which is well known as a non-renewable resource. An intense increase in the price of petroleum-based bitumen due to the depletion of petroleum reserves forces road authorities to explore alternative materials. Currently, the global practice is moving towards a sustainable, economical, and green environment. The scientific community is exploring the optimisation of bioresources in the pavement industry, driven by the benefits of renewability, sustainability, reduced costs, and lower energy consumption.

Biomass is the primary source of biomaterial, whereas biomass refers to living things that store solar energy, such as plants, animals, and microorganisms (Zhang et al., 2020). Among various forms of biomaterial, bio-oil is a widely accessible material and is categorised as waste oil from the forest/agriculture industry, animal, and residual. Hence, modifying the bitumen with bio-oil significantly minimises issues regarding non-renewability and fluctuation of bitumen cost (Wang et al., 2020). The compatibility and potential of bio-oil modified bitumen exhibit moderate satisfaction,

and their quality tends to vary based on the source and content (Aziz et al., 2015). However, the addition of agricultural waste oil (5–10 wt.%) improves the bio bitumen viscosity and low-temperature properties with marginal improvement in the high-temperature properties (Yang, 2013; Yang et al., 2013). Similarly, the waste wood oil-based asphalt mixture improved the anti-fatigue and crack resistance properties (Mohammad et al., 2013). Conversely, animal waste oil is commonly utilised less than 10 wt.% by asphalt to achieve better performance (Fini et al., 2011; Sun et al., 2017). The addition of animal waste based bio-oil reduces the viscosity and stability of asphalt at higher temperatures and increases low-temperature crack resistance (Fini et al., 2012). The refining of agricultural and animal-based oils involves time-consuming and costly procedures such as pyrolysis and hydrothermal liquefaction. (Rogers and Brammer, 2012; Zhang et al., 2020). In this way, the current implementation of bio-oil to modify bitumen is mainly focus on plant-based oil such as waste cooking oil/waste vegetable oil, as these soft oils are ready substrate with lower production cost (Al-Sabaei et al., 2020; Ramadhansyah et al., 2020; Wen et al., 2013; Zhang et al., 2020).

Waste cooking oil (WCO) is considered a potential bio-based waste material as it can lead to multiple topologies of the product (Mannu et al., 2020). WCO is generated after frying activities, and the rising population has increased its quantity due to the increased demand for food. WCO is related to the vegetable oil family and mainly arises from the kitchen and food industry. The global consumption of vegetable oil in 2023 has reached 213.08 million metric tons, and each year consumption is increasing by 2% as shown in Figure 1.1. In contrast, a significant problem regarding the proper disposal and collection of WCO is still unsolvable for a long time. The lack of

awareness and facilities, and improper disposal of WCO are leading to environmental, ecological and municipal problems (De Feo et al., 2020; Teixeira et al., 2018). Hence heavily consuming oil and fats, many countries face sewer blockage problems associated with an increased annual cost to remove blockage (Zhao et al., 2021).

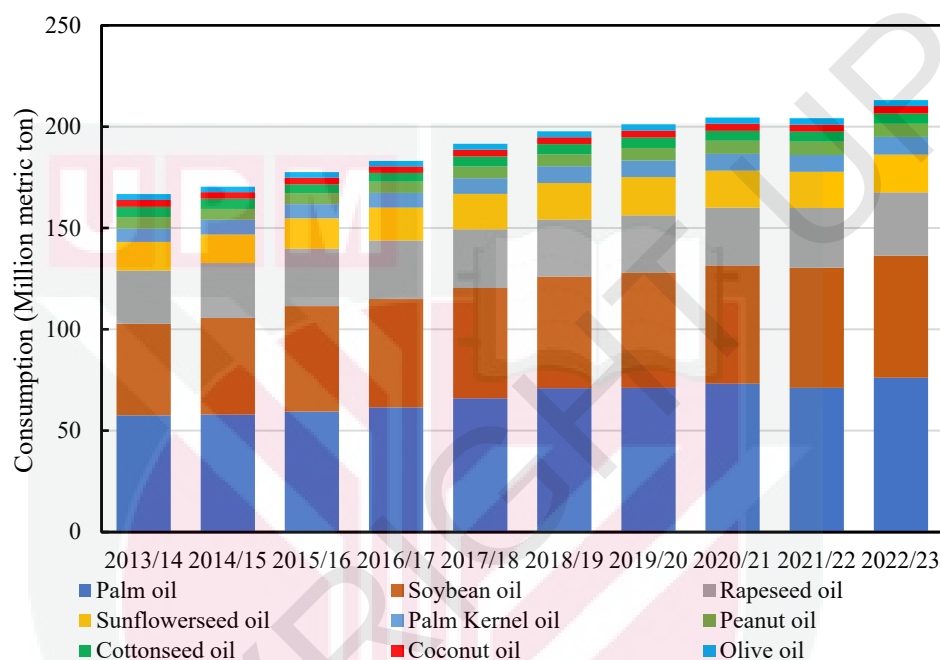


Figure 1.1: Global vegetable oil consumption Worldwide by oil type
(Source: Zahoor et al., 2021a)

One approach to solve this issue is to adopt a circular economy strategy for WCO by its reconversion that can reduce environmental impacts while increasing economic efficiency (Ramos et al., 2013). Recycling WCO provides a renewable feedstock for biofuels (i.e., biodiesel) and other bio-based goods (e.g., soap and animal feed) due to its chemical composition (Li et al., 2021). However, it also helps to minimise pollution by reducing greenhouse gases (GHG) produced by inappropriate handling (Tsai, 2019). A typical application of WCO as a modifier in the pavement industry dates back to 2013 since many studies were conducted in the laboratory to examine WCO-

modified bitumen performance (Azahar et al., 2016a; Wen et al., 2013). Based on previous research, it can be concluded that WCO is a potential waste material due to its consistent performance, specifically at low and intermediate temperatures (Asli et al., 2012; Azahar et al., 2016c; Zahoor et al., 2021a). On the other hand, high-temperature properties of WCO modified binders are still compromised as WCO can soften the bitumen which causes higher penetration and lower softening. Thus, it is believed that soft bitumen cannot withstand high-temperature exposure and leads to poor rutting resistance (Ramadhansyah et al., 2020; Rodrigues et al., 2020). The quality of WCO, which includes the acid value as a quality assessment parameter, influenced the high-temperature performance of the modified asphalt binder. The high acid value is associated with free fatty acid (FFA) and water content in WCO. However, the undesired characteristic of a high acid value limits the application of WCO as a bitumen modifier.

Azahar et al. (2016c) investigated the effect of acid value and water content on bitumen modification and revealed that chemically treated WCO with lower acid values and water content showed better high-temperature performance. However, the physical performance of treated WCO was still below the control binder and compromised. To overcome the deficiencies encountered by the WCO-modified binder, the researcher recently utilised additional modifiers such as waste polymers, palm oil fuel ash (POFA) and nano clay (NC). It was concluded that WCO modified bitumen with other modifiers could withstand hot climate regions. Moreover, a higher percentage of WCO can be used along with additional modifiers to enhance performance while ensuring a more sustainable environment (Adesina and Dahunsi, 2021; Khan et al., 2019; Niu et al., 2021a).

1.2 Problem Statement

In recent decades, rapid urbanisation and the rising number of vehicles have led to a surge in the need for road pavement construction and maintenance. Approximately 95% of global roads rely on flexible pavement, where conventional bitumen serves as the binding material. Since petroleum-based bitumen is non-renewable and finite, it is discouraged to use this material excessively. The pavement industry has taken sustainable approaches, and researchers have developed environmentally friendly bitumen, called bio-bitumen (Wen et al., 2013; Zhang et al., 2020). Thus, the current application of bio-bitumen is predominantly focused on plant-based oil such as waste cooking oil (WCO), as these waste oils are economical and ready substrates (Elahi et al., 2021; Ma et al., 2021; Sun et al., 2017).

WCO is abundant in households, restaurants, and food industries, generating about 15 million tonnes annually with a 2% yearly increase (Wang et al., 2020; Zahoor et al., 2021b). Its use as a bitumen modifier has gained attention, with numerous studies exploring its effectiveness (Abdalla et al., 2022; Wang et al., 2018; Wen et al., 2013; Zhang et al., 2020). Increasing WCO in bitumen improves thermal cracking resistance but reduces complex modulus (G^*) and decreases viscosity, limiting high-temperature performance. Consequently, only up to 2 wt.% WCO is recommended for hot regions.

Researchers suggest combining WCO with other modifiers to enhance stability at high temperatures (Dahunsi and Adesina, 2017; Maharaj et al., 2015; Niu et al., 2021b). Saboo et al.(2021a) found that nano clay (NC) had no significant effect on fatigue resistance in WCO-modified bitumen, recommending a maximum of 2.5 wt.% WCO with 6 wt.% NC for rutting resistance. Rahman et al. (2017) noted that using more than

5% WCO softens bitumen, making it unsuitable for warmer regions in conjunction with tire rubber powder (TR), and palm oil fuel ash (POFA). Similarly, Liu et al.(2020) reported the outcomes of styrene-butadiene-styrene and Ethylene-vinyl acetate (SBS-EVA) modified bitumen with 5% and 10% of WCO. The SBS-EVA-modified bitumen and 10% WCO showed slightly higher rutting deformation than the 5% modified bitumen. It is concluded that WCO reduces the viscosity, complex modulus (G^*), and creep stiffness of bitumen, compromising its performance at higher temperatures. Additionally, more than 2 wt.% WCO is not recommended for hot regions due to its softening effect, which makes it unsuitable for warmer climates. These limitations indicate the necessity of using additional modifiers like SBS to enhance the stability and performance of WCO-modified bitumen, particularly at high temperatures. This research focuses on the deficiencies that affect the WCO-bitumen modification and a new methodology has been developed to prepare an efficient novel dry modifier using the WCO in conjunction with the SBS at two different ratios. The WCO has caused the pre-swelling of the SBS and formed the rubbery-solid material. Conversely, a significant difference in molecular weight between SBS and bitumen leads to limited thermal compatibility, resulting in segregation issues (Zhang et al., 2022). To address this, a high-speed shearing technique is used to disperse SBS into bitumen, but it is energy-intensive and environmentally harmful (Oliviero Rossi et al., 2015). The high temperatures during transport also cause ageing and structural damage to SBS. Producing SBS-modified bitumen typically requires two to three hours of high-temperature shearing and development (Chen et al., 2021). Moreover, using WCO and SBS separately does not significantly improve bitumen performance. Therefore, the use of new composite material may shed some light on improving the modified bitumen performance and the blending process. This creates the source of motivation

for current research and to the best of the author's knowledge, no previous study has modified WCO in conjunction with SBS under dry modification to enhance the performance of the bitumen.

1.3 Objectives of the study

The study intends to investigate the effect of modified waste cooking oil on the bitumen and asphalt mixture performance characteristics. To achieve this aim, the following specific objectives are defined in this research:

1. To formulate the Styrene Butadiene Styrene (SBS) modified waste cooking oil granulates.
2. To evaluate the rheological, morphological and chemical properties of waste cooking oil granulate-modified bitumen.
3. To determine the optimal mix design for asphalt mixtures incorporating modified waste cooking.
4. To evaluate the mechanical performance of waste cooking oil granulate modified asphalt mixtures.

1.4 Scope and limitations of the study

This study involves an extensive literature search and laboratory testing to evaluate the effect of modified waste cooking oil on 60/70 grade bitumen properties. The waste cooking oil was subjected to modification to change its phase from liquid to semi-solid before being incorporated into the bitumen. The WCO was mixed with the SBS at five different ratios (SBS: WCO = 20:80, 30:70, 40:60, 45:55 and 50:50). These modified WCO ratios were assessed by blending with bitumen on trial and error basis. The optimal performing ratios were selected for further evaluation of bitumen and asphalt

mixture performance. This study provides a comprehensive examination of the influence of modified waste cooking oil granulates at ratios of 45:55 and 50:50 on the rheological, morphological, chemical, and mechanical performance of asphalt mixture. The William Landel Ferry equation was utilized to transform the rheological data for constructing master curves, and a sigmoidal model was employed to validate these master curves. Field Emission Scanning Electron Microscopy (FESEM) and Fourier Transform Infrared Spectroscopy (FTIR) were employed to examine the morphology and microstructure of the modified bitumens. Furthermore, in this research, AC-14 type Hot Mix Asphalt (HMA) was employed to assess the performance of the asphalt mixture with the incorporation of modified bitumen. Various tests, including stiffness modulus, Marshal stability, flow, Cantrabro test and dynamic creep were conducted to evaluate the performance characteristics of the asphalt mixture. Therefore, this study made a significant contribution to providing MWCO-modified bitumen and asphalt mixtures. It's important to acknowledge that the precision and applicability of the findings might have been influenced by certain potential limitations.

- The WCO is collected domestically and SBS was procured from Qastalani Sdn Bhd in Malaysia.
- The study focused on one type of 60/70 bitumen grade and an S/B block ratio (%) of 30/70.
- The study is conducted under controlled laboratory conditions.
- The one aggregate gradations and source (granite) are used to understand the behaviour of MWCO asphalt mixtures.
- The collected waste cooking oil (WCO) was used for various frying purposes, potentially containing residual ingredients, and its source was not well-defined.
- The small sample size with three replicates for each bitumen content may reduce the statistical power of the analysis.

The applicability of the findings from the study on MWCO-modified bitumen and asphalt mixes is limited, potentially impacting their broader implementation. To enhance the generalizability, it is advisable to consider a diverse range of WCO sources, bitumen qualities, and various types of SBS block ratios in a broader context. The variability in the SBS composition could affect the selected optimal ratios of MWCOG and overall performance of the modified bitumen. Additionally, the conclusions could benefit from utilizing multiple aggregate gradations and source types instead of relying solely on one aggregate type like granite. The residual substances remaining after the filtration process may alter the chemical composition of the WCO. Similarly, frying duration and heat intensity may also affect the chemical properties of the WCO. It is worthwhile to adopt a standardized chemical process to neutralize the chemical composition of all collected WCO. The study used three replicates for each bitumen percentage, which may limit the statistical power and the ability to detect smaller effects. A larger sample size could provide more robust results and improve the sensitivity of the analysis. This limitation should be considered when interpreting the findings, and future studies could address it by increasing the number of replicates. Furthermore, the controlled laboratory conditions may not perfectly reflect the actual field pavement performance. Thus, it is important to validate the laboratory results comprehensively, conducting tests on modified asphalt mixes in actual field conditions. The current study testing and analysis mainly focused on the same source for the materials with identical modification processes which ultimately did not significantly affect the validity of results in a broader context.

1.5 Novelty and contribution

This research aims to develop a novel modification of waste cooking oil by transforming the liquid phase of waste cooking oil (WCO) into a semi-solid structure. Also, the study seeks to investigate the impact of this novel modification on the properties of bitumen and asphalt mixtures. Furthermore, this study also assesses the effects of WCO modification on the homogeneity of the modified bitumen. The outcomes of this research have the potential to advance our knowledge and comprehension of modified WCO as a bitumen modifier, thereby encouraging its utilization as an eco-friendly material within the pavement industry.

The prospective advantages of incorporating waste cooking oil (WCO) in bitumen modification encompass enhanced recycling efforts and the mitigation of the substantial issue of proper disposal. In summary, this research holds the potential to offer valuable insights for the creation of more sustainable and efficient methodologies for bitumen modification within the pavement industry.

1.6 Thesis outlines

Aligned with the study's objectives, the research has been structured into five chapters, including this introductory chapter. Chapter 2 provides an extensive literature review pertaining to the production of the WCO, the physical and chemical properties of WCO and its interaction process with bitumen. Also, it presents the discussion on incorporating the different types of bio-oils into the bitumen in terms of its physical, rheological and asphalt mixture properties. Furthermore, Chapter 2 includes a

thorough discussion of bitumen's rheological properties and its ageing process. The mathematical model that was utilised to generate the master curve and the laboratory tests are also discussed. The design for the experimental tests and the materials used in the investigation are described in Chapter 3. Furthermore, Chapter 3 clarifies the stages involved in the experimental methods, the bitumen modification technique, and the modification of the WCO procedure. In Chapter 4, the experimental results are further analysed and discussed, and this is subdivided into two primary stages. The initial stage focuses on examining the characteristics of bitumen, its physical, and rheological properties, and microstructural tendencies. Conversely, the subsequent portion explores the performance attributes within asphalt mixtures. Lastly, Chapter 5 encapsulates the study's ultimate conclusions and offers suggestions for future research work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This Chapter presents the overview of waste cooking oil (WCO) and its utilisation for the improvement of performance for the pavement industry. The literature review primarily involves the physical and chemical properties of WCO. The production of the WCO and disposal concerns are discussed in this Chapter. The Chapter also discusses the chemical and physical changes during the frying activities and their post-effects on the bitumen properties. The conventional and rheological properties of the WCO modified bitumen with and without the additional additives have been discussed and summarised in this section. Also, the Chapter critically highlights the utilization, advancement, and challenges associated with the modification of bitumen using WCO. This Chapter also provides the comprehensive framework of the study which mainly highlights the potential gap of the study and possible solutions for the modification and phase change of the WCO. The last part of the literature review provides the characteristics of bitumen and its viscoelastic properties and the time-temperature superposition principles pertaining to the development of the rheological data master curve.

2.2 Waste cooking oil

Waste Cooking Oil (WCO), often referred to as used cooking oil, is a byproduct of culinary processes that holds significant environmental and economic potential. This

discarded oil, typically generated in households, restaurants, and food processing facilities, has traditionally posed disposal challenges as shown in Figure 2.1. However, with increasing awareness of its negative impact on the environment, there is a growing emphasis on recycling and repurposing waste cooking oil. The global consumption of vegetable oil in 2021 has reached 209.14 million metric tons, and each year consumption has increased by 2% (Saboo et al., 2021a). In contrast, the challenge of appropriately disposing of and collecting waste WCO has remained unresolved for a long time. The lack of awareness, facilities, and improper disposal of WCO are leading to environmental, ecological, and municipal problems. Consequently, due to the extensive use of oil and fats, numerous countries contend with sewer blockage issues, and approximately 40% of sewer system blockages can be traced back from improper waste cooking oil disposal in kitchen sinks (Zahoor et al., 2021b). This situation contributes to an increased annual cost of clearing these blockages.

One approach to solve this issue is to adopt a circular economic strategy for WCO by its reconversion, which can reduce environmental impacts while increasing economic efficiency (Ramos et al., 2013). Recycling WCO provides a renewable feedstock for biofuels i.e., biodiesel and other bio-based goods (soap and animal feed) due to its chemical composition (Li et al., 2021). Although, it also helps to minimize pollution by reducing greenhouse gases (GHG) produced by inappropriate handling (Tsai, 2019). Moreover, recycling waste cooking oil helps mitigate clogging issues in wastewater systems, making it an eco-friendly and cost-effective solution that exemplifies the principles of the circular economy.



Figure 2.1: Waste cooking oil
(Tsai, 2019)

2.2.1 Production of waste cooking oil

The vegetable oils market is dominated by palm and soybean oils, which account for 36% and 28% of the market. Other vegetable oil fractions include sunflower (9.09%), rape (13.2%), peanut (2.95%), corn (2.1%), coconut (1.75%), olive (1.48%) and sesame (1.1%) (Teixeira et al., 2018). Amongst all continents, Asia is on top of the list for higher production of vegetable oil. Domestically edible oil is used for frying purposes, whereas food processing industries and fast food companies use oil largely (Jamil et al., 2018). Frying is a process in which food is fried at a temperature between 150–200 °C in the presence of moisture, anti-oxidants and pro-oxidants (Safari et al., 2018). During frying, various reactions occur, such as hydrolysis, polymerization, isomerization, and oil decomposition. After a frying operation, the leftover oil is considered waste material and named waste cooking oil or used cooking oil (Koh and Surh, 2015). The rapidly growing world's population has dramatically increased the food demand which ultimately affects the production of WCO. Recent studies estimate that the generation of waste cooking oil is almost 20–32% of total edible oil

consumption (Cárdenas et al., 2021; Teixeira et al., 2018). China and India are the most populated countries and produce more WCO, around 5.6 million tons and 1.135 million tons per year. Canada, Denmark, Spain, Italy, Japan, South Korea, Malaysia and the United Kingdom have average generations, ranging from 0.1 – 0.5 million tons per year (Daud et al., 2020). The other remaining countries produce not more than 0.1 million tons per year and as per capita production of WCO, South Korea is on top of the list, followed by EU countries (Teixeira et al., 2018).

2.2.2 Physical and chemical properties of WCO

WCO is a thick dark brown or black liquid at room temperature and is considered an undesirable material as it is composed of complex organic compounds such as acids, ester, and aldehydes (Zahoor et al., 2021a). The composition and variation in organic compounds depend on the oil source and degradation reaction during frying activity (Choe and Min, 2007). The degradation reaction increases density, viscosity, specific heat, foaming and total polar material value of oil. Variation in viscosity and density of WCO varies due to the formation of other complex organic compounds such as glycerides, dimeric and polymeric acids (Tomasevic and Siler-Marinkovic, 2003).

Table 2.1 shows the physical properties of WCO.

Table 2.1: Physical properties of WCO

Reference	Viscosity@ 40°C (m ² /sec)	Density (g/cm ³)	Water content (%)
(Wen et al., 2010)	4.2×10 ⁻⁶	0.91	1.9
(Demirbas, 2009)	36.4×10 ⁻⁶	0.924	0.42
(Tomasevic and Siler-Marinkovic, 2003)	144.5×10 ⁻⁶ –	0.932–	–
	179.9×10 ⁻⁶	0.936	
(Phan and Phan, 2008)	30.5×10 ⁻⁶ –	0.920	–
	31.77×10 ⁻⁶		
(Dobromir Ivanov Jordanov , Petko Stoyanov Petkov, Yanko Kirov Dimitrov, 2007)	64.1×10 ⁻⁶	0.933	–
(Ramadhansyah et al., 2020)	4.9×10 ⁻⁶	0.9013	0.140

The major components of edible oil are triacylglycerol with fatty acids, with variable degrees of unsaturation, ranging from C16 to C18 carbon chain. Triglycerides are made by linking glycerol to three fatty acids, whereas all fatty acids contain an even no carbon chain (Cárdenas et al., 2021). Moreover, natural edible oil is also composed of other minor components such as free fatty acids (FFA), acylglycerols, carotenoids, tocopherols, tocotrienols, sterols, phosphatides, hydrocarbons, and trace metals (Shahidi, 2004). For the preparation of food, deep-frying is one of the traditional and widely used methods. While frying at high temperatures such as 150 – 200 °C, food reacts to heated oil, air, and moisture present in food. Thus, hydrolysis, oxidation and polymerization are common reactions and produce volatile and non-volatile compounds (Table 2.2) (Choe and Min, 2007). Therefore, it is concluded that the chemical and physical changes during deep-frying affect the overall composition of waste cooking oil from that of edible oil, as shown in Figure 2.2.

Table 2.2: Variation in the chemical composition of oil after the frying process

Chemical Reaction	Reason of reaction	Variation in chemical composition
Hydrolysis	Water, steam, Oxygen	Production of di.mono-acylglycerols, glycerol, and free fatty acids
Oxidation	Surrounding air or oxygen	Production of CO, CO ₂ , and dimeric compounds
Polymerization	Heating oil at high-temperature range 260 °C – 340 °C	Formation of dimers including oligomers that increase the molecular weight of oil

(Azahar et al., 2016c)

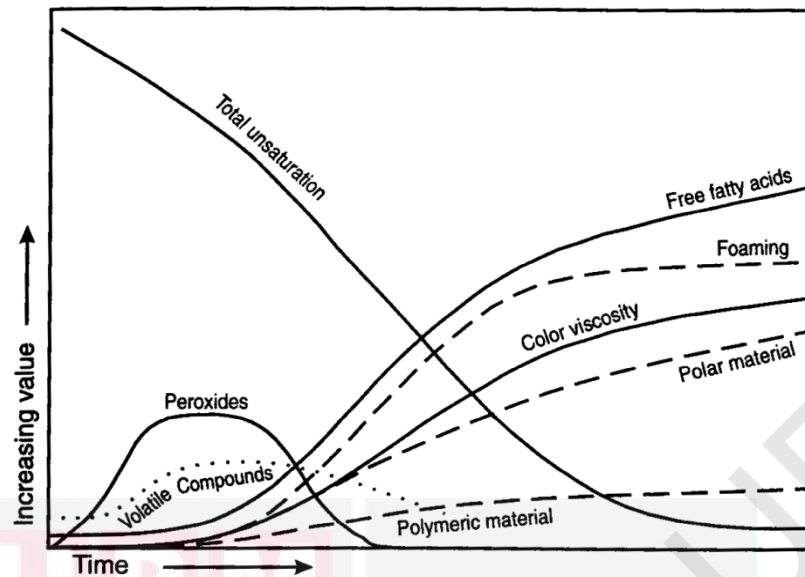


Figure 2.2: Physical and chemical changes in oil during deep-frying
(Choe and Min, 2007)

2.2.3 Free fatty acid (FFA) in WCO

The edible oil undergoes chemical and physical changes during frying activities, and the quality of oil degrades. The steam generation during the frying reacts with the oxygen and water in the food, initiates the hydrolysis process, and produces the FFA. The concentration of the FFA varies and depends on diverse conditions such as heating temperature, moisture content, and storage time. Thus, with the additional reaction time the triglyceride bonds break down and produce FFA, including glycerol, di, and monoglycerides, as shown in Figure 2.3. Furthermore, at a temperature above 150 °C, the glycerol accelerates the hydrolysis process, leading to further FFA production (Naz et al., 2005). As the degradation process continues, the production of FFA accelerates, which ultimately decreases the unsaturation level of cooking oil. Hence, the oil becomes no longer suitable for further frying and needs to be discarded as waste material (Zhang et al., 2012).

The WCO quality can be monitored by the acid value parameter, which identifies the concentration of FFA and the amount of water content (Ahmed and Hossain, 2020; Zahoor et al., 2021a). However, the researcher has utilized the gas chromatography-mass spectrometry (GC-MS) technique to analyze the concentration of FFA in WCO. The acidic compounds of WCO are categorized as saturated, monounsaturated, and polyunsaturated compounds. The chemical composition of WCO studied by Azahar et al. (2017) indicated that Palmitic acid, stearic acid, and meristic acid are examples of saturated fatty acids. Whereas monounsaturated fatty acids contain oleic acid, cis-11-eicosenoic. Table 2.3 indicates that the main components of WCO are oleic acid, palmitic acid, and linoleic acid, which account for 43.67%, 38.35%, and 11.39%, respectively (Asli et al., 2012; Zahoor et al., 2021a).

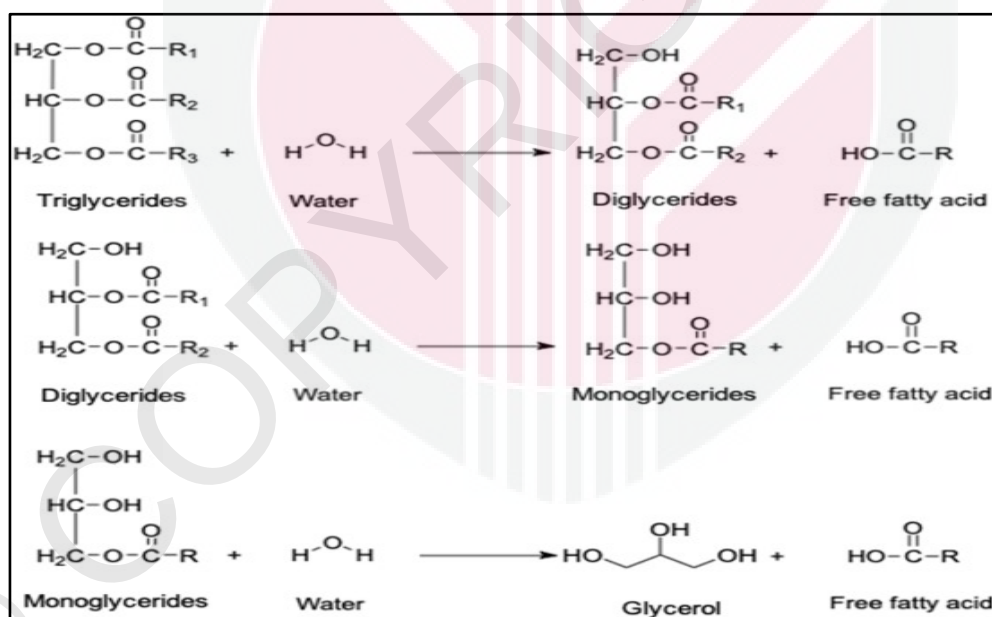


Figure 2.3: Chemical composition of WCO
(Zahoor et al., 2021a)

Table 2.3: Hydrolysis of triglycerides

Formulation of Fatty Acids	Type of Free Fatty Acid	Possible % in Waste Cooking Oil (WCO)	Type of Saturation
C18:1 (Cis 9)	Oleic Acid	43.67	Unsaturated
C16:0	Palmitic acid	38.35	Saturated
C18:2 (Cis)	Linoleic acid	11.39	Unsaturated
C18:0	Stearic acid	4.33	Saturated
C14:0	Myristic acid	1.03	Saturated
C18:3 alpha	γ- Linolenic acid	0.37	Unsaturated
C12:0	Lauric acid	0.34	Saturated
C18:2 t	Linolenic acid	0.29	Unsaturated
C20:1	Cis-11-Eicosenoic acid	0.16	Unsaturated
C21:0	Heneicosanoic acid	0.08	Saturated
TOTAL		100	

(Houhoula et al., 2003)

2.3 Application of WCO as bio-bitumen in pavement industry

A typical approach to preparing a bio-asphalt binder is simply blending biomaterial (such as WCO) with asphalt. The bio-asphalt binder is further classified into three categories based on oil content in a binder (Table 2.4). However, 100% replacement of conventional binder to bio-asphalt binder is not suggestible as the saturates, aromatics, resins, and asphaltenes (SARA) fraction of traditional asphalt and bio-oil is not similar. In addition, the volatile matter and water content in bio-asphalt binders could negatively impact the performance and durability of the asphalt mixture (Aziz et al., 2015). Therefore, bio-asphalt can be used as a modifier or extender.

Table 2.4: Classifications of bio-bitumens

Category of application content in the binder	Content in the binder	Current State
Modifier	<10%	The application mode is relatively mature
Extender/substitute	25%–75%	The application mode is common
Alternative	100%	The application mode cannot be achieved due to the limitation of the performance of bio-asphalt

Initially, the WCO was utilized as a rejuvenator due to its oily nature for aged asphalt. It has the potential to restore low molecular weight compounds and viscosity lost due to the ageing of a binder. Similarly, following this attempt researchers started exploring the opportunity of using WCO as a modifier to improve asphalt binder (Asli et al., 2012; Azahar et al., 2016c; Su et al., 2015; Wen et al., 2013; Zargar et al., 2012). The modification of the asphalt binder with WCO needs proper blending variables. However, there is no specific standard available for the WCO modified asphalt.

Table 2.5 lists primary preparation variables such as shear time, speed and temperature in producing the WCO modified binder. Su et al. (2018) reported that the higher mixing temperature and shearing rate could generate a suitable vortex for WCO blending with asphalt binder. On the other hand, Wang et al. (2014) stated that mixing variables should not exceed the specified limit as too high a temperature and shearing rate for a long duration could destroy the quality of WCO-modified binder. Therefore, the literature concluded that the most utilized mixing condition of WCO in asphalt binder uses a shear rate of less than 5000 rpm at 135 °C–160 °C for about 30–60 min.

Table 2.5: Mixing variables for WCO modified binder

Reference	Shearing time (min)	Shearing speed (rpm)	Shearing temperature (°C)
(Luo et al., 2017)	50	4000	170
(Azahar et al., 2016a)	60	1000	160
(Somé et al., 2016)	30	–	190
(Al-Omari et al., 2018)	5.0	1600	145
(Azahar et al., 2017)	60	1000	160
(Wang et al., 2018)	30	4000	140
(Azahar et al., 2016c)	60	1000	160
(Eriskin et al., 2017)	60	4000	160
(Rasman et al., 2018)	60	1000	163
(Erman ÇAVDAR, Aytuğ KUMANDAŞ, 2019)	120	2000	150

Table 2.6: Summary of the reviewed literature on the use of WCO and additives at various concentrations

Reference	Modifier	Content of WCO/additives (wt.%)	Penetration (dmm)	Viscosity @ 135 °C (Pa.s)	Softening point (°C)	Ductility (cm)	Rutting resistance (Pa)	Fatigue resistance (Pa)	Low temperature stiffness (Mpa)
(Wen et al., 2013)		10, 30, 60	↑	↓	↑	—	↑	↑	↑
(Somé et al., 2016)		17.9	↑	—	↑	—	↑	—	↑
(Al-Omari et al., 2018)		1, 2, 4, 6, 8	↑	↓	↑	—	↑	↑	↑
(Maharaj et al., 2015)	Simply filtered WCO	10	—	↓	↑	—	↑	↑	—
(Azahar et al., 2016a)		3, 4, 5	↑	↓	—	—	↑	—	—
(Eriskin et al., 2017)		1, 3, 5	↑	↓	—	—	↑	—	—
(Rasman et al., 2018)		1, 2, 3	↑	↓	—	—	↑	—	—
(Bilema et al., 2019)		2, 4, 6	↑	↓	—	—	↑	—	—
(Azahar et al., 2016c)	Chemically treated WCO	—	↓	—	—	—	↑	—	—
(Nordiana et al., 2019)		3, 4, 5	—	—	—	—	↑	—	—
(Luo et al., 2017)	SBS/PE/WCO	5, 5, 5	↓	↑	—	↑	↑	—	↓
		5, 3	—	—	—	—	—	—	—
		5	—	—	—	—	—	—	—
(Adesina and Dahunsi, 2021)	HDPE/WCO	2, 5, 5, 7, 5	↓	—	↑	—	—	—	—
		5, 10, 15	—	—	—	—	—	—	—
(Niu et al., 2021a)	GTR/WCO	10, 15, 20	↓	↑	↑	↑	↑	↓	↓
		2, 5, 5, 7, 5, 10	—	—	—	—	—	—	—
(Joni et al., 2020)	LDPE+PVC/WCO	1, 3, 5	↓	↑	↑	↑	—	—	—
		1, 2, 3	—	—	—	—	—	—	—
		5	—	—	—	—	—	—	—
(Rahman et al., 2017)	WCO/TR/POFA	5, 7, 5, 10	↑	↑	↓	—	↑	↑	—
		5, 7, 5, 10	—	—	—	—	—	—	—
(Saboo et al., 2021b)	NC/WCO	2, 4, 6	↔	↓	↓	—	↑	↔	—
(Erman ÇAVDAR, Aytuğ KUMANDAŞ, 2019)	WCO in SBS-modified binder	2, 5, 5, 5	↑	↓	↓	↔	—	—	—
		1, 3, 5, 7, 9	—	—	—	—	—	—	—
(Liu et al., 2020)	SBS/EVA/WCO	3, 5	↓	↑	↑	↑	↑	↑	↑
		5, 5	—	—	—	—	—	—	—
		5, 10	—	—	—	—	—	—	—
(Khan et al., 2019)	WCO/TR/Bagasse	5, 10, 15, 20	↑	↑	↑	—	↑	↑	↑
		5, 8, 12, 15, 18	—	—	—	—	—	—	—
(Dahunsi and Adesina, 2017)	HDPE/WCO	7, 7, 7, 5, 8, 10	↓	—	↑	—	—	—	—
		2, 5, 5, 7, 5	—	—	—	—	—	—	—
		5	—	—	—	—	—	—	—

(↑) Increase in properties, (↓) decrease in properties, (↔) no change in properties

2.3.1 Effect of WCO on conventional properties of bitumen

The incorporation of WCO at various concentrations affects the physical properties of WCO-modified asphalt binder as shown in Table 2.6. Thus, higher concentration increases the penetration while effectively reducing modified asphalt consistency (Azahar et al., 2017). According to the conclusions drawn by Al-Omari et al. (2018), the penetration was observed to increase when 1–8 wt.% of filtered WCO was added to 76–145 dmm asphalt compared with the penetration the 65 dmm of the neat asphalt. Consequently, the softening point results have followed a similar trend with decreased temperature to 44 °C compared to 53 °C neat asphalt. A similar study was conducted by Eriskin et al. (2017) in which asphalt was modified by adding 1–5 wt.% of WCO to asphalt. The experimental outcomes have shown an increase in the penetration resistance to 102 dmm on a high content of the WCO when using a grade 50/70 asphalt. Similarly, the softening was reduced from 52.1 to 43.3 °C on high usage of WCO. Also, Somé et al. (2016) utilized the WCO and reported a decrement in penetration and softening point results. The dilution of WCO distributes the asphalt particles more uniformly, which lowers the interaction between the saturation level of WCO and binder and can significantly lower the grades of a modified binder. Thus, many researchers have suggested that filtered WCO-modified binder could perform better in the cold region than conventional base asphalt (Zargar et al., 2012).

On the other hand, the quality of WCO has a significant role in asphalt binder modification. The higher acid value of WCO weakens the bond between WCO and asphalt binder, as discussed in previous sections. In this way, Azahar et al. (2016a) evaluated the effect of acid values on the performance of modified asphalt. The WCO

samples from April, August, and December were used with acid values of 3.5, 2.8, and 1.6 mL/g, respectively. The 60/70 base asphalt was replaced by 3–5 wt.% of a binder. It was noticed that penetration was minimal for December compared to the other samples due to its lower acid value. Similarly, in another study, Azahar et al. (2016c) used treated WCO (transesterification) and compared the performance with untreated WCO in asphalt binder. The 28, 46, and 52% reduction in penetration was observed while adding treated WCO by 3, 4, and 5 wt.%, respectively. However, the results of the softening points are directly proportional to the penetration resistance, and improvement of 3, 4, and 5% was noted compared to the untreated WCO modified bitumen (Figure 2.4a). The improved penetration value indicates that chemically treated WCO modified binder is much harder than untreated WCO modified binder due to strong interaction bonding between saturation level of treated WCO and asphalt binder (Ahmed and Hossain, 2020). Therefore, the chemical treatment of WCO might be a valuable alternative for WCO-modified asphalt binder in hot climate regions.

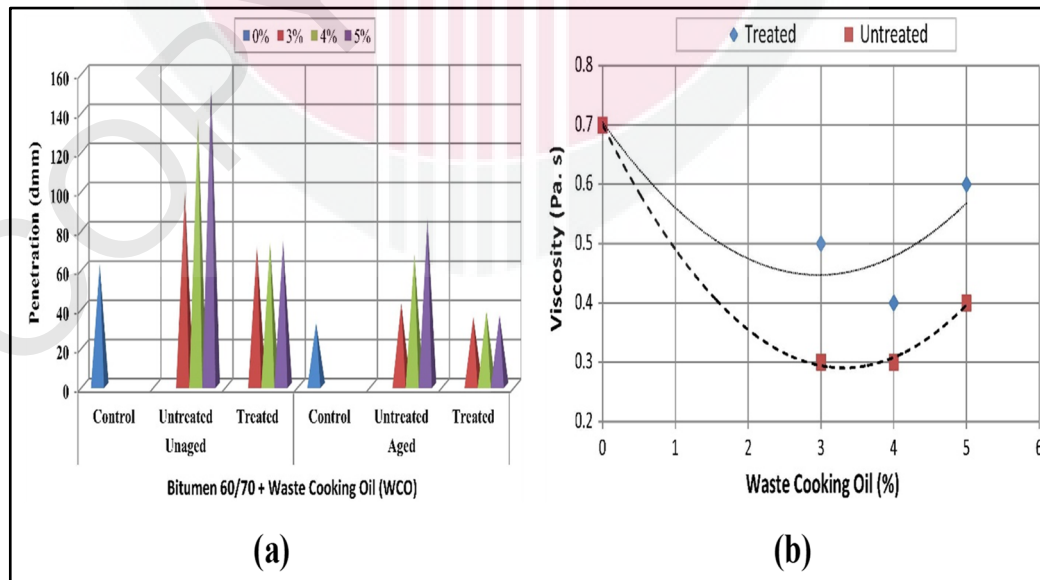


Figure 2.4: Effect of WCO content on bitumen: (a) Penetration, (b) Rotational viscosity
(Azahar et al., 2016c)

Further reviewing the WCO modified asphalt binder, the flow characteristic is worth considering. Rasman et al. (2018) studied the viscosity of the untreated WCO modified asphalt binder. Hence results revealed that the rotational viscosity at 135 °C was decreased linearly with an increase in the dosage of the WCO. Thus, the lowest viscosity was 0.2 Pa s for 3% WCO compared to 0.3 Pa s of the neat asphalt. Similar results were reported by Bilema et al. (2019) while adding the WCO at 2–6 wt. % of the 60/70 asphalt binder. The viscosity was reduced to 0.388 Pa s compared to the viscosity of a neat asphalt binder of 0.628 Pa s. Similarly, in studies by Al-Omari et al. (2018) and Mahrez et al. (2009), incorporating the untreated WCO softens the binder and reduces the viscosity. Thus, it is perceived that the WCO without proper treatment to reduce the acid values caused the asphalt binder to soften and ultimately declined the performance. The reduction in the consistency of the asphalt binder is due to the dilution and less internal friction; thus, there is an inverse relationship between the viscosity of the asphalt binder and the content of WCO.

Consequently, Azahar et al. (2016a) used different months of samples of WCO from April, August, and December to modify asphalt binder. The results indicated that the lower acid value sample of December showed some enhanced viscosity at 135 °C compared to other samples of WCO modified asphalt binder. Azahar et al. (2016c) followed the transesterification process to reduce the WCO acid value. It is noticed from the outcomes that the viscosity of the treated WCO modified asphalt binder is 33% improved than the untreated modified binder. However, WCO at 5 % replacement can also be observed that viscosity has shown an increasing trend as shown in Figure 2.4b. The viscosity increment at 5% is attributed to the adhesiveness between the particles of WCO and asphalt binder with no dilution effect. From an economic

standpoint, the marginal reduction in the viscosity is favourable for the ease of mixing and compaction temperature and to save the cost

2.3.2 Effect of WCO on rheological properties of bitumen

The asphalt binder demonstrates the viscoelastic properties and mainly depends on the temperature and the frequency variation. The rheological properties are characterized by the complex modulus (G^*) and the phase angle (δ). The dynamic shear rheometer is widely used to identify the shear resistance of the asphalt binder. The G^* refers to the total resistance of the asphalt binder against deformation generated by shear loading, whereas the δ refers to the time delay between shear strain and shear stress. For a better understanding, the WCO modification and its effect on the viscoelastic behaviour of the asphalt binder are worth analyzing. Thus, Bilema et al. (2019) studied the G^* and δ of the untreated WCO modified asphalt binder. They observed the decline in the values of G^* for the WCO content of 2–6 wt.% of the asphalt. The G^* values were more pronounced at a temperature range of 46–58 °C particularly on the higher dosage of the WCO. It elucidated that the G^* of the 6% WCO modified asphalt was reduced by 84% compared to the without modification. However, the G^* has not shown any notable difference in the values at a higher temperature. On the contrary, the δ is approaching the 90° on increasing content of WCO which indicates the shift towards the viscous behaviour of asphalt binder. In other comprehensive studies by Somé et al. (2016) and Wen et al. (Wen et al., 2013), the performance of untreated WCO modified asphalt binder on the higher content has similar trends of the G^* and δ as concluded by (Bilema et al., 2019).

The rutting ($G^*/\sin\delta$) and fatigue ($G^*\cdot\sin\delta$) parameters are the evaluation indicators for determining high and intermediate temperature resistance as per the super pave specification, respectively. The reflective values to resist against the load for the $G^*/\sin\delta$ and the $G^*\cdot\sin\delta$ should be greater than 1.0 KPa and equal to or less than 5000 KPa, respectively. In a recent study by Al-Omari et al. (2018), the $G^*/\sin\delta$ was evaluated by adding untreated WCO 1–8 wt.% of the asphalt binder. The results indicated that the increasing content of the WCO reduces the failure temperature of the modified asphalt. Figure 2.5a shows a slight variation in the $G^*/\sin\delta$ up to 4% of WCO and satisfying the Super Pave criterion. However, on the higher content of untreated WCO, the $G^*/\sin\delta$ of the modified asphalt dropped drastically. The reduction in the $G^*/\sin\delta$ at higher content of WCO for asphalt binder modification was also reported by Rasman et al. (2018). The results indicated that $G^*/\sin\delta$ is nearly similar to WCO modified asphalt binder at lower content; however, there was a sudden reduction in values on incorporating higher content of WCO as shown in Figure 2.5b. Nordiana et al. (2019) reported a reduction in the $G^*/\sin\delta$ on incorporating WCO more than 5 wt. % of the asphalt binder similarly to (Al-Omari et al., 2018; Rasman et al., 2018).

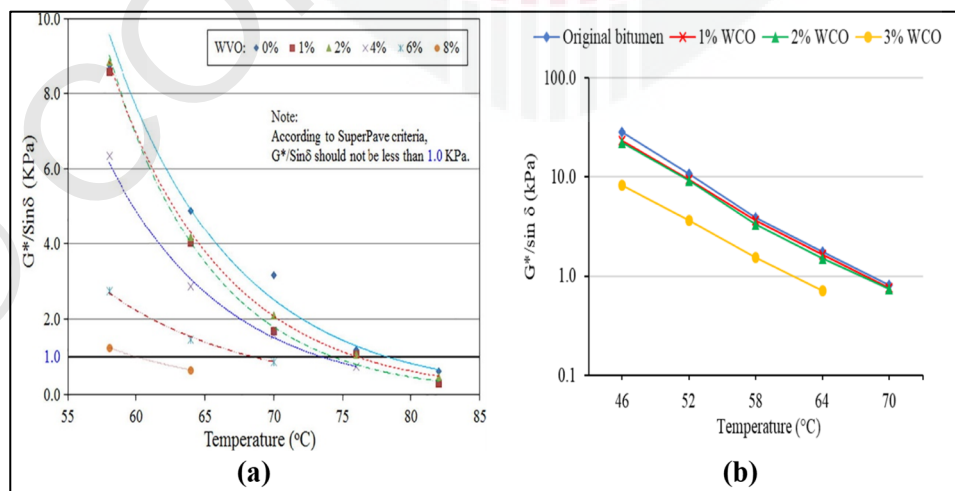


Figure 2.5: Rutting parameters of asphalt binders at various content of WCO (Al-Omari et al., 2018; Rasman et al., 2018)

The quality of the WCO greatly influences the rutting performance of the WCO modified asphalt binder, and acid value is the key parameter. In another study, Azahar et al. (2016c) evaluated the $G^*/\sin\delta$ by incorporating the three different qualities of WCO with acid values of 3.5, 2.8, and 1.6 mL/g. The results imply less $G^*/\sin\delta$ of 1.6 mL/g acid value WCO modified asphalt compared to 3.5 mL/g. The failure temperature was 64 °C for the 1.6 mL/g acid value WCO modified asphalt, which is higher than the 58 °C, and 58.2 °C for 3.5 and 2.8 mL/g acid value WCO modified asphalt, respectively. Azahar et al. (2016c) recently employed the transesterification process to treat WCO and significantly reduce the acid values from 1.66 to 0.54 mL/g. The treated and untreated WCO modified asphalt binder failed at 70 °C and 64 °C, respectively (Figure 2.6). It was observed that the chemical modification of WCO improves the quality of WCO, which ultimately enhances rutting resistance. Acid values improvement provides better chemical bonding between WCO and base binder, producing a stiffer WCO modified asphalt binder (Sun et al., 2016; Zhang et al., 2017, 2020).

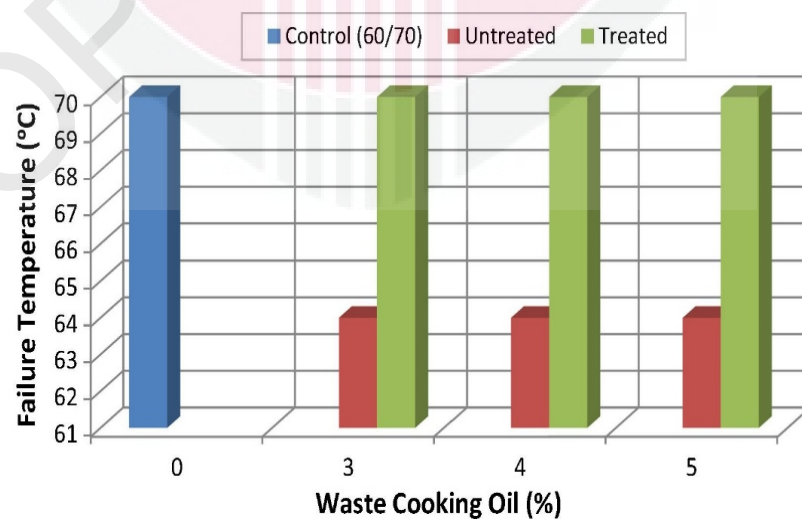


Figure 2.6: Failure temperatures of untreated and treated modified asphalt binders
(Azahar et al., 2016c)

Apart from the higher temperature (rutting resistance), the intermediate temperature (fatigue resistance) also significantly impacts the performance of the WCO modified asphalt binder. Usually, fatigue damage occurs in pavements due to repeated load and propagates within the bitumen mastic, resulting in microdamage. WCO can modify the asphalt binder and disperse energy by rebounding and without cracking the pavements due to improved adhesion. Al-Omari et al. (2018) reported on the $G^* \cdot \sin \delta$ and exhibited that as the WCO content increases fatigue resistance decreases at the intermediate temperatures compared with the neat asphalt binder. The reduction in the $G^* \cdot \sin \delta$ for modified asphalt binder with WCO 1–8 wt.% at 28 °C was 9%–33%, respectively. Hence, the adding of WCO can enhance fatigue resistance. Similarly, in other studies by (Cao et al., 2019; Maharaj et al., 2015), WCO can increase fatigue resistance at intermediate temperatures, and WCO modified binder has improved performance than a base binder.

Al-Omari et al. (2018) investigated further WCO modified asphalt binder and revealed that WCO enhances the binder elasticity at low temperatures. The S-values of the modified asphalt with WCO decreased and met the super pave criterion at -6 and -12 by 45% and 54%, respectively. Yet, there are pronounced changed m-values when more than 4% WCO was incorporated into the asphalt binder. Similarly, other comprehensive studies by Sun et al. (2016), Gong et al.(2016), Zhu et al.(2017), and Zhang et al. (2017) supported the same result of WCO- modified binder in low temperature. It has been shown that adding more WCO improves the creep stiffness, whereas the m-value decreases. The lower temperature makes the binder stiffer, and light components in WCO can soften the binder and the m-value increases. On the other hand, due to the hydrolysis process, the presence of water content has a negative

effect on the quality of WCO and compatibility of asphalt binder with WCO which consequently affects the low-temperature properties of WCO modified asphalt binder. Thus, the WCO refinery must control the moisture content using any water removal method to enhance the properties of the WCO-modified asphalt binder (Hong et al., 2020).

Generally, these studies constantly revealed that WCO changes the rheological characteristics of asphalt binders. The incorporation of WCO lowered the shear strength and decreased the resistance to flow. Therefore, based on the results of rheological tests, it can be inferred that using WCO as a modifier offers superior fatigue resistance and low-temperature performance. However, reducing rutting resistance may cause concerns, which may be addressed by modifying WCO chemically or physically by adding other polymers as modifiers such as SBS, LDPE, and GTR. could be a better alternative for ensuring practical application.

2.3.3 Effect of WCO with additional additives on conventional properties

The incorporation of untreated and treated WCO in asphalt binder has been investigated by several researchers and observed an insignificant improvement in the physical and rheological performance (Al-Omari et al., 2018; Azahar et al., 2016c; Bilema et al., 2019; Nordiana et al., 2019). For instance, the chemically treated WCO performs better in comparison to the untreated WCO. However, further enhancement was made when the researcher utilized other additional modifiers in conjunction with the WCO, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), ground tire rubber (GTR), nano clay (NC). Adesina and Dahunsi (2021)

studied the effect of WCO and HDPE as a modifier on the physical properties of asphalt binder. The penetration resistance increased by 20.7% by adding WCO 15 wt.% of asphalt. Incorporation of the WCO softens the asphalt thus causing a decrement in softening properties by 41%. However, the reduction in physical properties was counter balanced by adding the HDPE (Figure 2.7). The 11.6% reduction in penetration resistance and 37% increase in softening point was observed on adding HDPE 7.5 wt.% of asphalt.

Similarly, Joni et al. (2020) studied the influence of LDPE and PVC on the WCO (1 wt.%) modified asphalt binder. The results indicated that adding PVC and HDPE 5 wt.% of WCO modified asphalt decreased the penetration by 31% and 33%, respectively. The softening point trends were in a similar manner with an enhancement of 7.2% and 7.4% compared to WCO 1 wt.% modified asphalt binder results. Another similar study by Dahunsi and Adesina (2017) investigated the physical properties of WCO modified asphalt binder in conjunction with HDPE. The results were similar to those by (Adesina and Dahunsi, 2021; Joni et al., 2020). The HDPE significant tolerance to high temperatures makes the gel type structure within the binder, thereby enhancing the modified binder's elastic properties.

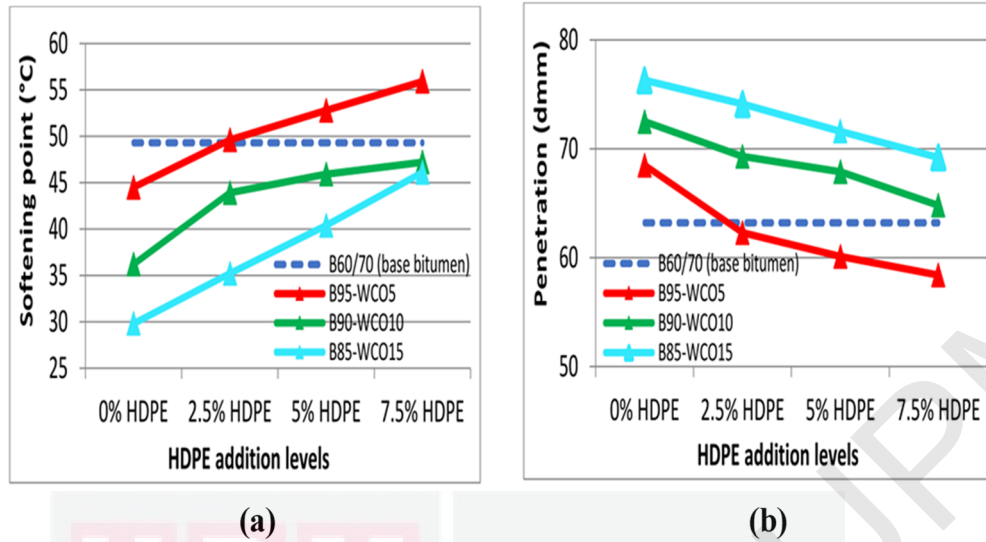


Figure 2.7: Effect of WCO and HDPE contents on asphalt binder: (a) softening, (b) Penetration resistance
(Adesina and Dahunsi, 2021)

In a recent study by Niu et al. (2021a), the effect of adding WCO (2.5–10 wt.%) of asphalt in conjunction with GTR (10–20 wt.%) of asphalt on rotational viscosity at 135 °C of binder was analyzed. The results indicated that the viscosity of WCO/GTR modified asphalt increased with increasing the dosage of GTR. The asphalt with 20% GTR has shown significant improvement with different contents of the WCO and temperature. Also, the increasing content of the WCO in GTR modified asphalt lowers the viscosity from 8 to 2.5 Pa s which signifies that the WCO causes a reduction in the compaction and mixing temperature of the mixture (Figure 2.8). A similar enhancement in the binder's viscosity by incorporating the WCO, GTR and POFA was reported by (Rahman et al., 2017). The results implied that the 15% replacement of composite material to asphalt resulted in enhanced rotational viscosity. The 5% WCO, 10% GTR and 7.5% POFA was the optimal combination which increased the 60% viscosity of asphalt compared to neat asphalt. High POFA and tire rubber powder make the binder viscous since they remain solid even as the temperature rises. Similarly,

Khan et al. (2019) also reported a similar result considering improving the viscosity of WCO/tire rubber(TR)/bagasse fiber-modified binder. Bagasse fiber was added as an additive. It was observed that due to the presence of tire rubber and bagasse fiber, almost 20% of base binder could easily be replaced by composite material, which will minimize environmental degradation caused by improper waste disposal.

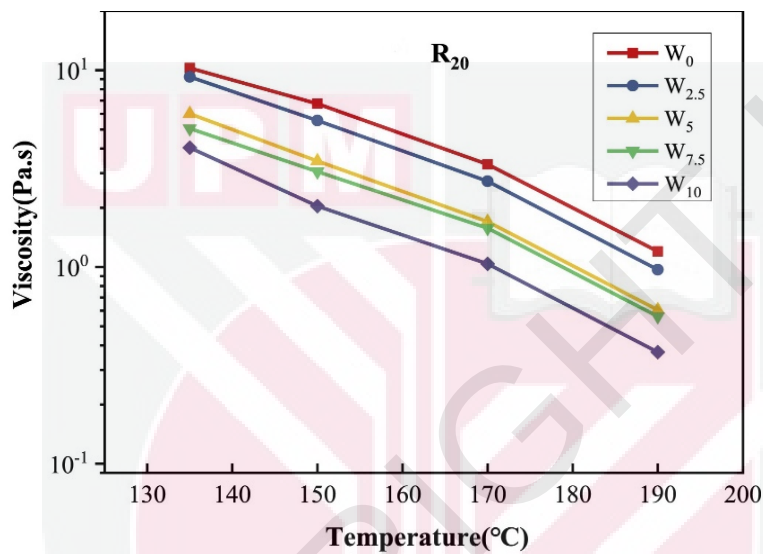


Figure 2.8: Effect of WCO and GTR content on the rotational viscosity at 135 °C (Niu et al., 2021a)

The addition of nano clay (NC) in the WCO-modified asphalt binder also positively impacted the softening point. The WCO 2.5% wt. and 6% dosage of NC the high-temperature base binder PG 70 improved to PG 76. This demonstrates that NC has a higher specific surface area, leading to an increase in stiffness of WCO-modified binder (Saboo et al., 2021b). Consistently, Styrene-butadiene-styrene (SBS) and Ethylene-vinyl acetate (EVA) can improve low-temperature deformation by increasing the ductility value of asphalt binder. A study conducted by Liu et al. (2020) investigated the change in the physical behaviour of SBS/EVA- modified asphalt and it was concluded that by addition of 10% WCO in SBS/EVA-modified binder

improved ductility value. This explains that SBS and EVA make a crosslinking translation in asphalt which allows for utilisation of more quantity of WCO and collectively leads to a pronounced increase in ductility value.

Other comprehensive studies by Luo et al. (2017) and Oruc (2019), reported the experimental findings of improving the ductility of SBS/LDPE modified asphalt with the incorporation of WCO, which demonstrated that adding WCO with polymers can increase flexibility and low-temperature fracture resistance. However, it is evident that the viscosity of WCO is lower; thus, the addition of WCO in the binder makes it more prone to rutting at a higher temperature. To fill this gap, researchers combined different additional modifiers such as waste plastic or other polymers with WCO to make a composite material and replaced different percentages of a base binder with composite material. This new study not only solved the issue regarding adhesive performance of asphalt binder but also worked well as an eco-friendly renewable binder in the pavement industry (Khan et al., 2019; Nassar et al., 2020; Rahman et al., 2017).

2.3.4 Effect of WCO with additional additives on rheological properties

The impact of composite materials on the high, low, and intermediate temperature properties of WCO-modified binder is shown in the previous Table 2.6. Multiple Stress Creep Recovery (MSCR) and Linear Amplitude Sweep (LAS) have gained popularity in testing rutting resistance and fatigue behaviour of asphalt binder using DSR (Jia et al., 2014; Saboo et al., 2021b; Wen et al., 2013). Whereas a few studies evaluated the rutting and fatigue properties of WCO-modified binder through MCSR and LAS tests. MSCR provides two essential characteristics to describe the reaction of a modified

asphalt binder under stress: non-recoverable creep compliance (J_{nr}) and percentage recovery (%) (Zahoor et al., 2021b). The Increased J_{nr} indicates weak thermal resistance to stresses and low bitumen rutting resistance (Wen et al., 2013).

Saboo et al. binder (2021b) revealed that J_{nr} varies in response to changes in the percentages of WCO and NC. A higher concentration of WCO responded to increased J_{nr} value due to the binder softening resulting from the addition of WCO. On the other hand, the value of J_{nr} dropped as the proportion of NC increased which simultaneously improved the rutting resistance of the modified binder. Yet at the higher temperature, NC can retain elasticity, thus improving the rutting resistance of NC/WCO-modified binder. Similarly, Niu et al.(2021a) reported the J_{nr} value of the GTR/WCO-modified binders under a single creep stress level (3.2KPa); results showed that WCO and GTR exhibit opposing impacts on the J_{nr} (3.2) value of the binder, suggesting that the negative effect of WCO on binders' rutting resistance can be balanced by properly increasing GTR content.

The (LAS) test is conducted to measure the potential of fatigue cracking at intermediate temperature caused by a repeated load with a linear amplification of strain at a constant frequency. The test consists of two stages: (1) a frequency sweep test to determine the alpha “ α ” parameter for damage analysis, and (2) an amplitude sweep test to assess damage buildup in the samples versus loading cycles. Niu et al. (2021a) demonstrated the fatigue life of GTR/WCO-modified binder at 2.5% and 5% strain levels. It was found that at a strain level of 2.5%, modified asphalt binder with 5wt% WCO and 20wt% GTR enhances the fatigue life by 9.6 and 4.6 times longer than 10 and 5 wt.% GTR as shown in Figure 2.9. Similarly, Saboo et al.(2021b) quantified the

fatigue behaviour of NC/WCO-modified asphalt binder. Based on the evaluation of stress versus strain, it was observed that the addition of NC in WCO-modified binder has no substantial effects on the fatigue resistance of asphalt binder at intermediate temperature. However, an increase in the percentage of NC leads to an increase in the small stiffness of the binder, thus increasing strain susceptibility.

Consequently, Rahman et al. (2017) reported the $G^*/\sin \delta$ and $G^*\sin \delta$ performance of 50 wt.% and 30 wt.% replaced base binder by tire rubber TR and WCO (under different percentage combinations). At the same time, POFA was added as a stabilizer in a modified binder. The presence of WCO enforced the modified binder particularly close to 80/100 binder. The result concluded that all modified samples exhibit poor resistance against rutting and higher fatigue resistance compared to base binder 60/70. Furthermore, few other studies observed a mixed trend of rutting and fatigue parameters of modified binder incorporation WCO with additional modifiers (Khan et al., 2019; Liu et al., 2020; Luo et al., 2017).

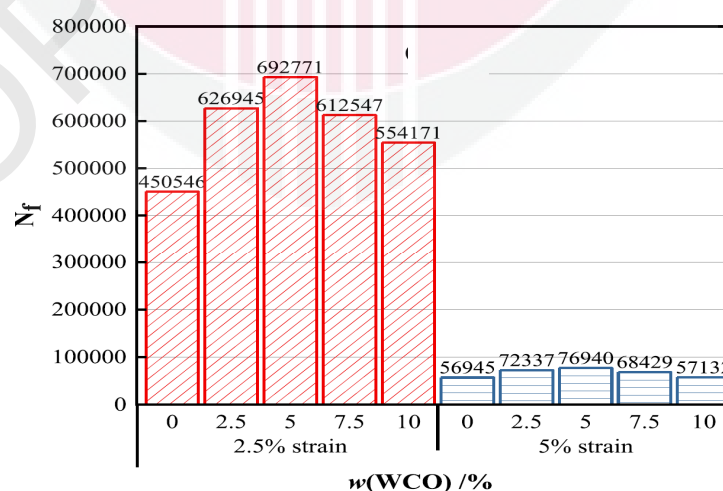


Figure 2.9: Predicted fatigue life of WCO and GTR modified bitumens (Niu et al., 2021a)

In conclusion, limited studies are available in terms of MSCR and LAS testing on WCO-modified binders. Adding WCO to the binder softens it, thus offering fatigue enhancement. Whereas non-recoverable creep compliance lowers permanent deformation resistance. As a result, to improve rutting resistance additional additives or composite materials should be considered before including WCO into the binder, with cautions based on the site's climatic circumstances.

Furthermore, Liu et al. (2020) reported the SBS and EVA modified asphalt outcomes in conjunction with the WCO. The low-temperature property of the modified binder was compromised and does not appear to enhance the performance. However, SBS/EVA can increase rutting resistance at high temperatures. Thus, when 5 wt.% and 10 wt.% WCO were mixed with SBS/EVA-modified asphalt, the asphalt met the Superpave requirements at -18°C and -12°C, test temperatures respectively (Figure 2.10). These findings show that WCO increases low-temperature fracture resistance significantly. This is because WCO-modified binder is softer than polymer-modified asphalt binder. Furthermore, similar results have been observed by (Khan et al., 2019; Niu et al., 2021a). For instance, Niu et al. (2021a) compared 10 wt.% GTR-modified binder with and without the addition of WCO; thus, it was deduced that the creep with higher WCO and GTR was deduced stiffness decreased whereas m-value increased. The addition of WCO accounted for the soft asphaltene absorbed by GTR, allowing GTR to play a more elastic supplemental function while improving low-temperature relaxation properties. As a result, the WCO/GTR-modified asphalt demonstrates satisfactory deformation ability at low temperatures. It can be inferred that adding WCO to the asphalt binder enhances thermal cracking resistance. Although blending, and concentration of WCO with other types of composite material affect both creep stiffness and m-value.

Researchers have conducted studies on the performance analysis of the WCO modified asphalt binder and in conjunction with other additives. The enhancement was demonstrated in the rutting and fatigue performance of the treated and composite asphalt binder. A study was conducted by Wen et al. (2013) to evaluate the influence of WCO on the rutting performance of the asphalt mixture. It was evaluated that the rutting potential of asphalt mixes reduces with a high dose of WCO using a dynamic repeated creep load. These findings support what was previously stated for the simply filtered WCO-modified binder rutting tests, based on complex shear modulus, phase angle and J_{nr} (Somé et al., 2016). On the other hand, Azahar et al. (2017) reported that the permanent deformation of WCO-modified mixture could be improved by chemically treating WCO.

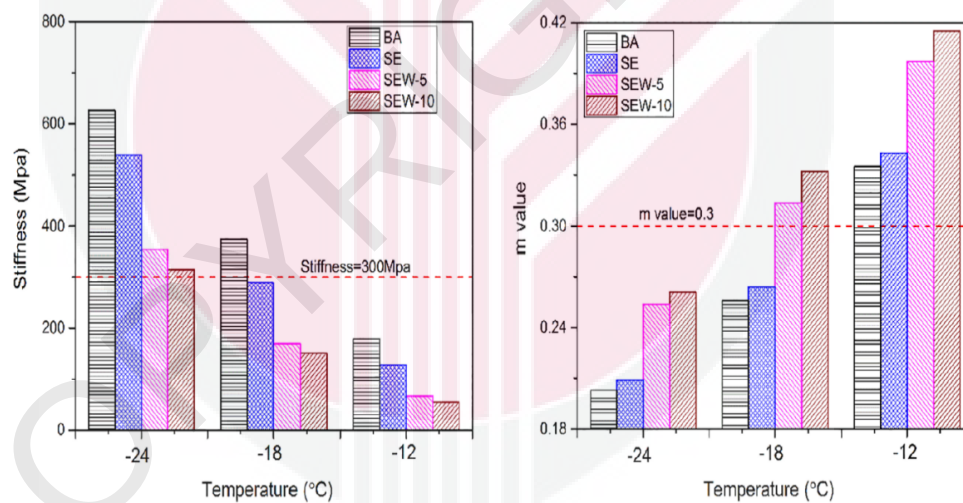


Figure 2.10: Creep stiffness and m-value of WCO and SBS/EVA modified bitumen
(Liu et al., 2020)

2.3.5 The impact of WCO on the performance of asphalt mixtures

Hence, the result indicated that at 40°C, after chemical modification of WCO the strain rate was reduced by 17.5% relative to the control mixture. The non-polar group in the

untreated WCO converts into a polar group, and polar attraction between treated WCO molecules and polar aggregate surface improves adhesion bonding thus, resulting in improved rutting resistance performance in asphalt mixture (Guarin et al., 2016). Furthermore, Niu et al. (2021a) performed a permanent deformation test by Dynamic Stability (DS) to demonstrate the dynamic stability of three mixes at high temperatures of 60 °C, and the results are shown in Figure 2.11. In comparison to the original asphalt mixture, the WCO-modified asphalt mixture showed less dynamic stability. Hence, the WCO/GTR-modified asphalt mixture has a much higher average dynamic stability than the other two asphalt mixes.

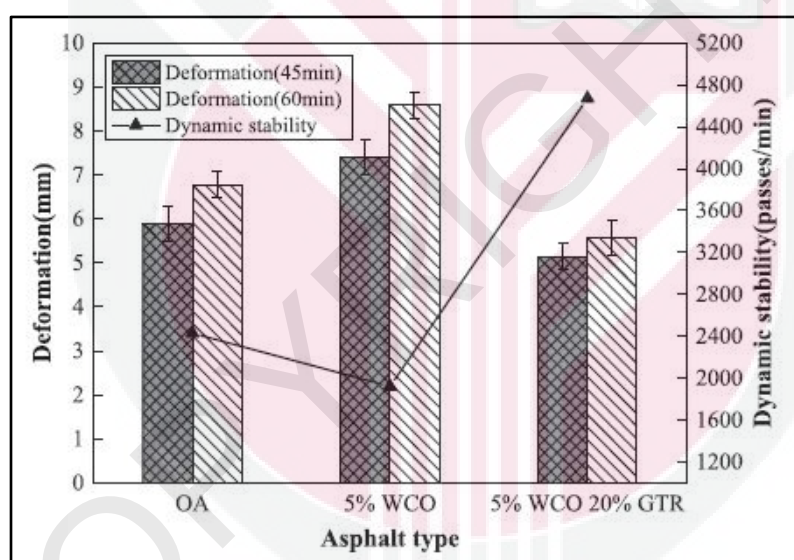


Figure 2.11: Marshal stability of asphalt mixtures
(Niu et al., 2021a)

The presence of WCO reduces the high-temperature performance of the asphalt mixture, whereas the addition of GTR counteracts the negative effects. The ability of GTR to modify the viscoelasticity of asphalt through physical and chemical interactions, results in a mixture with high stiffness and modulus that effectively reduces deformation under load. A similar result was identified by (Sun et al., 2017)

for optimized bio-asphalt (OBA), Pen 70 and SBS-modified mixture. However, it was observed from Figure 2.12 that all mixtures satisfy the critical high-temperature dynamic stability value 2400 times/mm for OBA and 800 times/mm for SBS-modified asphalt mixture. OBA contains different polymer concentrations along with WCO, which stiffens the binder and improves rutting resistance compared to the WCO-modified mixture. On the other hand, the addition of WCO into asphalt mixture has a positive impact on fatigue resistance whereas excessive dose may reduce the fatigue resistance of asphalt mixtures (Zaumanis et al., 2014).

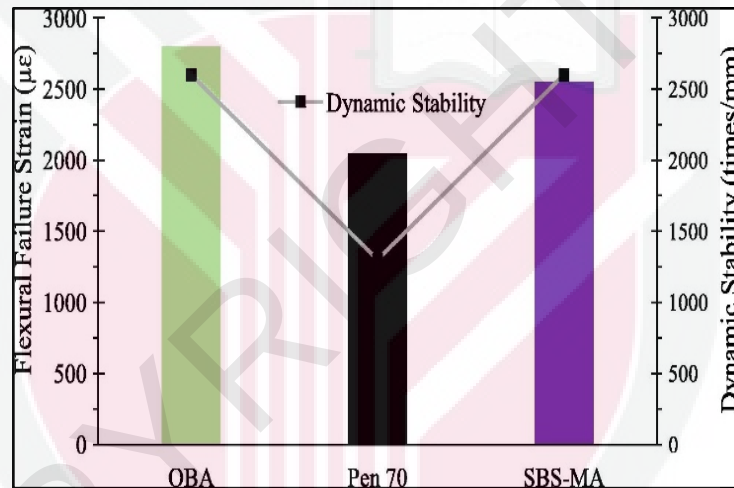


Figure 2.12: Dynamic stability of different HMA
(Sun et al., 2017)

Wen et al., (2013) revealed fatigue test results and indicated that as the amount of WCO in the mixture increases, asphalt fatigue decreases. On the other hand, an incremental dose of WCO enhances the resistance to thermal cracking indicated by a strength test at low temperatures. Similarly, three-point bending tests revealed that WCO-based asphalt mixes had a high flexural failure strain (5200 $\mu\epsilon$) when compared to control asphalt mixtures (2300 $\mu\epsilon$) and WCO/GTR modified asphalt mixtures (5000 $\mu\epsilon$). This suggests that WCO can increase the deformability of asphalt at low

temperatures and that adding GTR to the mix will reduce the effect of WCO. This demonstrates that a WCO-based asphalt mixture is resistant to low-temperature cracking (Sun et al., 2017). It is concluded the high concentration of WCO reduces the cohesiveness of asphalt binder which causes specimens to fail at lower deformations, resulting in less fatigue resistance. At the same time, it improves the asphalt mixture thermal cracking resistance. Although very limited studies are available on fatigue and thermal resistance of WCO-modified asphalt mixtures. Besides the mechanical performance of the WCO-modified mixture, the asphalt pavement with weak moisture resistance may experience moisture damage which ultimately affects the traffic flow, safety and limited service life in future (Zhang et al., 2020).

Wen et al. (2013) investigated the effect of simply filtered WCO addition on the moisture susceptibility of asphalt mixes and concluded that all samples containing WCO met the AASTHO Tensile strength ratio (TSR) minimum requirements (i.e. > 80%). However, similar results reported by (Eriskin et al., 2017), TSR values for each sample prepared with WCO were in the acceptable range. It is worth noting that moisture susceptibility depends on adhesion between asphalt and aggregate surfaces. WCO-modified asphalt mixture showed better TSR value than WCO/GTR-modified mixture which identifies adhesion bond between asphalt and aggregate. The adhesion is correlated with the quality of WCO. The presence of FFA in WCO may enhance the water affinity for the binder, resulting in increased moisture susceptibility. It has been noticed that linoleic acid and hexadecenoic acid are water-insoluble fatty acids and can easily be absorbed effectively in dry conditions. Thus, in a wet environment, these fatty acids are immediately replaced by water molecules and in return raise moisture susceptibility (Fini et al., 2020; Hung et al., 2019). It can be inferred from summarized

studies that WCO modified asphalt mixtures may fulfil the specification criteria. However, the impact of WCO on moisture susceptibility varies, depending on the individual mix and quality of WCO. Thus, it is needed to have an in-depth analysis of WCO modified mixture performance prediction.

2.3.6 Fourier transform infrared spectroscopy of WCO modified bitumens

Fourier Transform Infrared Spectroscopy is used to identify the characterization and identification of functional groups in the various samples (FTIR). The only analytical approach operates at room temperature while simultaneously monitoring the vibrations of the functional groups that describe the molecular structure (Chen et al., 2014). According to a previous experimental study, the area between 2.5 mm and 25 mm (4000 to 400 cm^{-1}) is the most acceptable for chemical investigation. Oldham et al. (2021) showed FTIR of untreated and chemically treated WCO. The absorbance peaks at 1446 cm^{-1} and 1196 cm^{-1} are attributed to $-\text{CH}_3$ and $\text{O}-\text{CH}_3$ stretching, which is noticed only in the case of treated WCO. However, the absence of glycerol peak at 1377 cm^{-1} detected esters in large abundance by area in treated WCO Figure 2.13. According to Wang et al. (2020), the presence of many ester substances in WCO can effectively improve adhesion between WCO-modified asphalt and aggregate. Besides this, Azahar et al. (2016b) observed one peak in untreated WCO-modified binder at 1743 cm^{-1} which shows the presence of $\text{C}=\text{O}$ bond which is a type of aldehyde and ketone bonds. This kind of bond forms due to the oxidation process that occurs in the WCO sample during the frying process. This peak softens the binder, making it more prone to rutting. In another study by Azahar et al. (2016c), it was revealed that with the chemical modification of WCO the $\text{C}-\text{H}$ bond and the $\text{C}=\text{C}$ stretch aromatic bond

increased for all percentages of treated WCO and C=O bond at 1743cm^{-1} was noticed as negligible. Thus, from the analysis of the above studies, it can be observed that by chemical modification of WCO the peak of C=O can be reduced drastically, resulting in enhancement of physical and rheological properties of WCO-modified asphalt binder which ultimately enhances the performance of asphalt mixture.

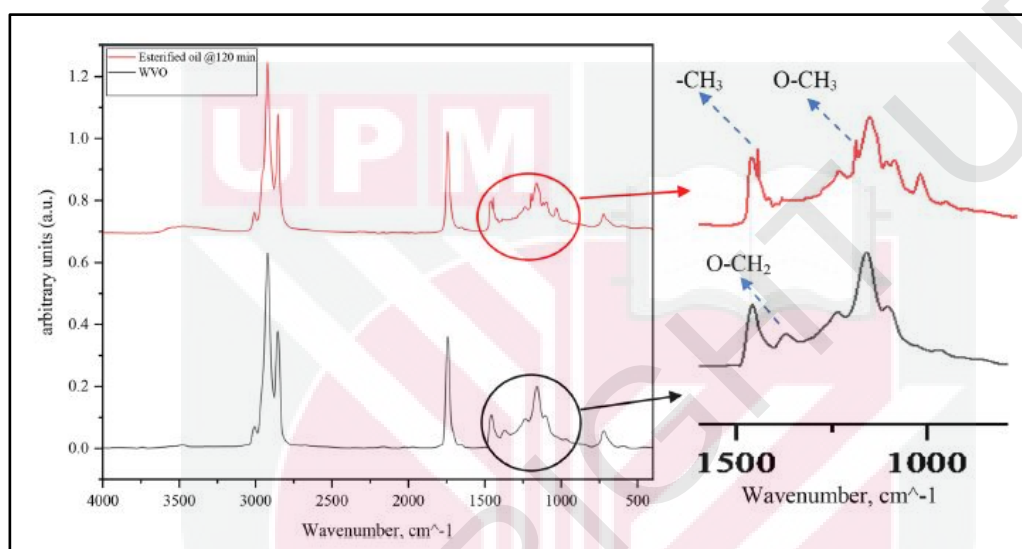


Figure 2.13: FTIR spectra of untreated and chemically treated WCO (Oldham et al., 2021)

2.4 Theoretical framework of the study

The comprehensive literature review conducted in previous sections serves as the foundation for the theoretical framework, built upon the synthesis of relevant existing concepts related to the research questions. The principal goal of this study is to use waste cooking oil (WCO) to enhance bitumen properties, thus improving performance. Numerous previous studies have demonstrated the promising impact of WCO on the modification of bitumen and asphalt mixture on certain properties. It is evident that the use of WCO enhances low-temperature performance but may not address high-

temperature properties adequately. For example, studies conducted by Wen et al. (2013) and Maharaj et al. (2015) have shown that incorporating WCO as a modifier in asphalt binder modification leads to a decrease in rutting resistance performance at high temperatures.

However, the decrease in rutting resistance may raise concerns and prompt the need for more in-depth explorations. One promising avenue to address this concern is the potential chemical or physical modification of WCO. This entails considering the incorporation of other polymers as modifiers, such as SBS (Styrene-Butadiene-Styrene), LDPE (Low-Density Polyethylene), or GTR (Ground Tire Rubber). Taking into account the comprehensive literature review and identified shortcomings, it is imperative to modify raw waste cooking oil (WCO) with a suitable polymer or hardener to induce a phase change before it can be effectively utilised for bitumen modification. Therefore, SBS has been recognized as the most suitable polymer for use in combination with WCO to induce a phase change in the oil.

Theoretical consideration of WCO-SBS and bitumen interaction

Styrene butadiene styrene (SBS), a member of the thermoplastic block copolymer family, possesses a biphasic morphology characterized by the presence of rigid polystyrene (PS) blocks connected by rubbery polybutadiene (PB) blocks (Schaer et al., 2017). This unique structure allows SBS copolymers to exhibit a cross-linked elastomer network behavior across a wide temperature range, primarily due to the significantly different glass transition temperatures of 95°C and 80°C for PS and PB respectively. These blocks are capable of deformation when subjected to tension and subsequently return to their initial shape once the stress is released (Li et al., 2022). In

the production of SBS, both linear (1D) and radial (2D) configurations can be achieved, and the butadiene-to-styrene (B:S) ratio is adjustable as shown in Figure 2.14.

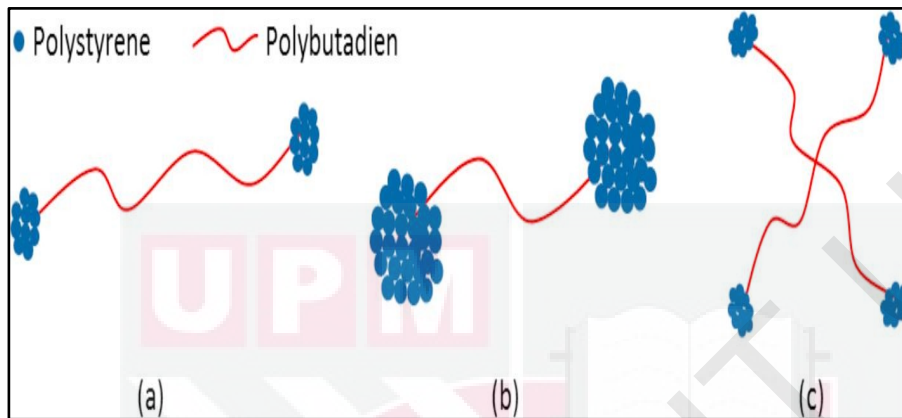


Figure 2.14: Illustration of SBS (a) linear SBS with high butadiene (b) with high styrene (c) radial SBS molecule (Schaur et al., 2017)

SBS-modified bitumen mixtures have been extensively employed in road construction due to their exceptional stability in both hot and cold temperatures, and their resistance to rutting. With its unique combination of qualities, SBS is ideally suited for modifying bitumen. When SBS copolymers are blended with bitumen, a biphasic microstructure emerges within the system. In this structure, the polymer-rich phase forms through the interaction of maltenes and the expanding polymer particles, dispersing within the asphaltene-rich phase (Luo et al., 2022a). However, a significant difference in molecular weight in SBS modifiers and asphalt is the reason for their limited thermal compatibility with each other. The introduction of SBS directly into the bitumen results in significant segregation issues, which detrimental effect on its overall quality. To address this issue, a high-speed shearing technique is employed during the traditional wet modification process to break down SBS and disperse it into the

bitumen. Nevertheless, this method is technologically deficient, consumes considerable energy costs and contributes to environmental pollution. The influence of SBS into the bitumen is illustrated in Figure 2.15.

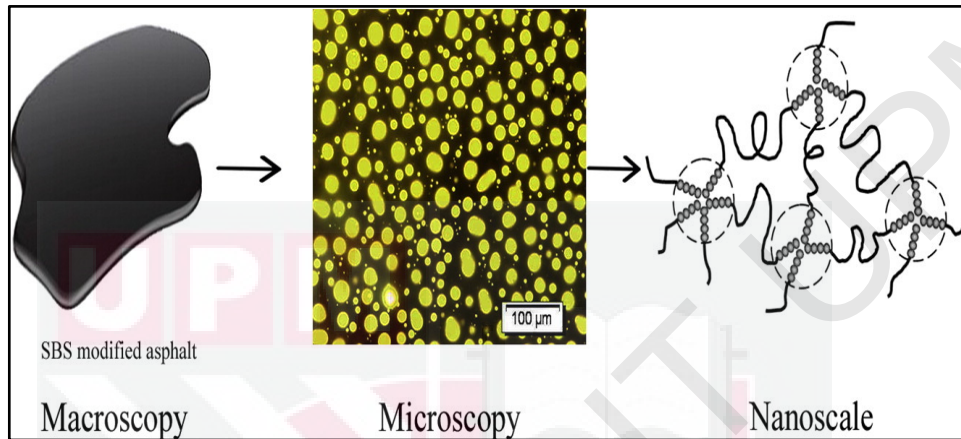


Figure 2.15: Schematic illustration of SBS influence on bitumen
(Schaur et al., 2017)

The technical drawbacks are the following: as soon as high-speed shearing is stopped, SBS begins to precipitate which will have a detrimental effect on the stability of the modified bitumen. This effect becomes more pronounced as the storage time increases. The constant high temperature conditions during the transport of modified bitumen result in ageing and structural damage to SBS. From an energy and environmental point of view, approximately two to three hours of high temperature shearing, swelling, and development are required to produce modified bitumen through the conventional modification process (Chen et al., 2021). To maintain the higher temperature conditions, fuel consumption is therefore required to be significantly increased which results in significant energy and greenhouse gas emissions. This situation has a significant impact on the environment. However, utilizing WCO and SBS separately for modification purposes does not significantly enhance the

performance of bitumen. Therefore, addressing this issue, the current study has identified a new approach to address the deficiencies of both WCO and SBS in bitumen modification.

In the pavement industry, there is a shift towards simplifying bitumen modification, reducing energy consumption, and promoting environmental sustainability. Researchers aim to develop materials that can be easily blended with bitumen and aggregates. On the other hand, the omission of the high-speed shearing step in the direct modification material technique can lead to uneven dispersion of SBS within the bitumen, consequently compromising the efficiency of the modification process. As a result, the necessary standards for modified bitumen cannot be met. Conventional research suggests that the modification process involving SBS and bitumen entails a physical reaction during heating, which leads to stable 3D network structures. This modification process comprises two main components. Firstly, the butadiene block (PB segment) within SBS absorbs the lighter components of bitumen, resulting in swelling and an expansion of the PB blocks volume. Secondly, the styrene block (PS) in SBS undergoes crosslinking with bitumen (Sun et al., 2017).

Therefore, considering the above theoretical concepts relating to the WCO and its effects on the bitumen and asphalt properties. The SBS was chosen to modify the phase change of WCO to a rubbery solid state. The phase change possibly causes the enhancement in the homogeneity of the modified bitumen with better adhesion. Pre-swelling of SBS in WCO enhances the rapid and uniform dispersion of SBS in bitumen. Following swelling and absorption of the lighter components of WCO, a cross-linking phenomenon takes place, promoting adhesion and compatibility between

WCO and SBS. These cross-linking reactions further enhance the three-dimensional network structure in the modified bitumen and make the modified waste cooking oil more stable.

2.5 Summary

This Chapter extensively reviewed the literature and the experimental evidence on utilising WCO for the improvement of the bitumen and asphalt mixture properties. The previous studies majorly focus on the WCO in raw form as a bitumen modifier. Whereas, fewer have utilised other waste polymers in conjunction with the WCO to enhance the performance of bitumen and asphalt mixtures. However, the oily phase of the WCO has restricted the enhancement and the higher incorporation of the WCO into the bitumen. As it directly causes a reduction in the stiffness of the bitumen and asphalt mixtures. Therefore, the pre-modification of the WCO is desirable to change its oily phase to a rubbery solid state. Also, the potential polymer has been identified in this Chapter to be used in the modification of the WCO to produce the modified WCO. In the forthcoming Chapter, the focus will be on the methodology for modifying waste cooking oil (WCO) with styrene-butadiene-styrene (SBS) and determining the optimum ratio of WCO to SBS. The chapter will also explore various experimental methods to assess the impact of this modified mixture on bitumen and asphalt performance.

CHAPTER 3

METHODOLOGY

3.1 Introduction

Following a thorough review of the literature in Chapter 2, the methodology for achieving the research objectives was formulated. This study was conducted to provide a comprehensive evaluation of the impact of waste cooking oil on the rheological properties of bitumen. Additionally, morphological analysis, chemical analysis, and the determination of phase separation were undertaken to further substantiate the study's objectives. Additionally, an asphalt mechanical performance test was conducted to assess the performance of the bitumen modified with waste cooking oil (WCO). The four proportions (5%,10%,15% and 20%) of the two modified waste cooking oil (MWCO) ratios were incorporated into the 60/70 penetration-grade bitumen to achieve the objectives. The granite aggregate was used for the preparation of the asphalt mixtures for the mechanical performance analysis by employing the HMA AC14 gradation. Figure 3.1 depicts the methodology and experimental approaches of the study as per the objectives while each objective is expanded further with more thorough flow charts. In summary, this chapter offers a thorough discussion of the experimental plan organized according to the study objectives. It emphasizes the materials employed, the process of specimen preparation, and the testing of these materials in accordance with established standard procedures.

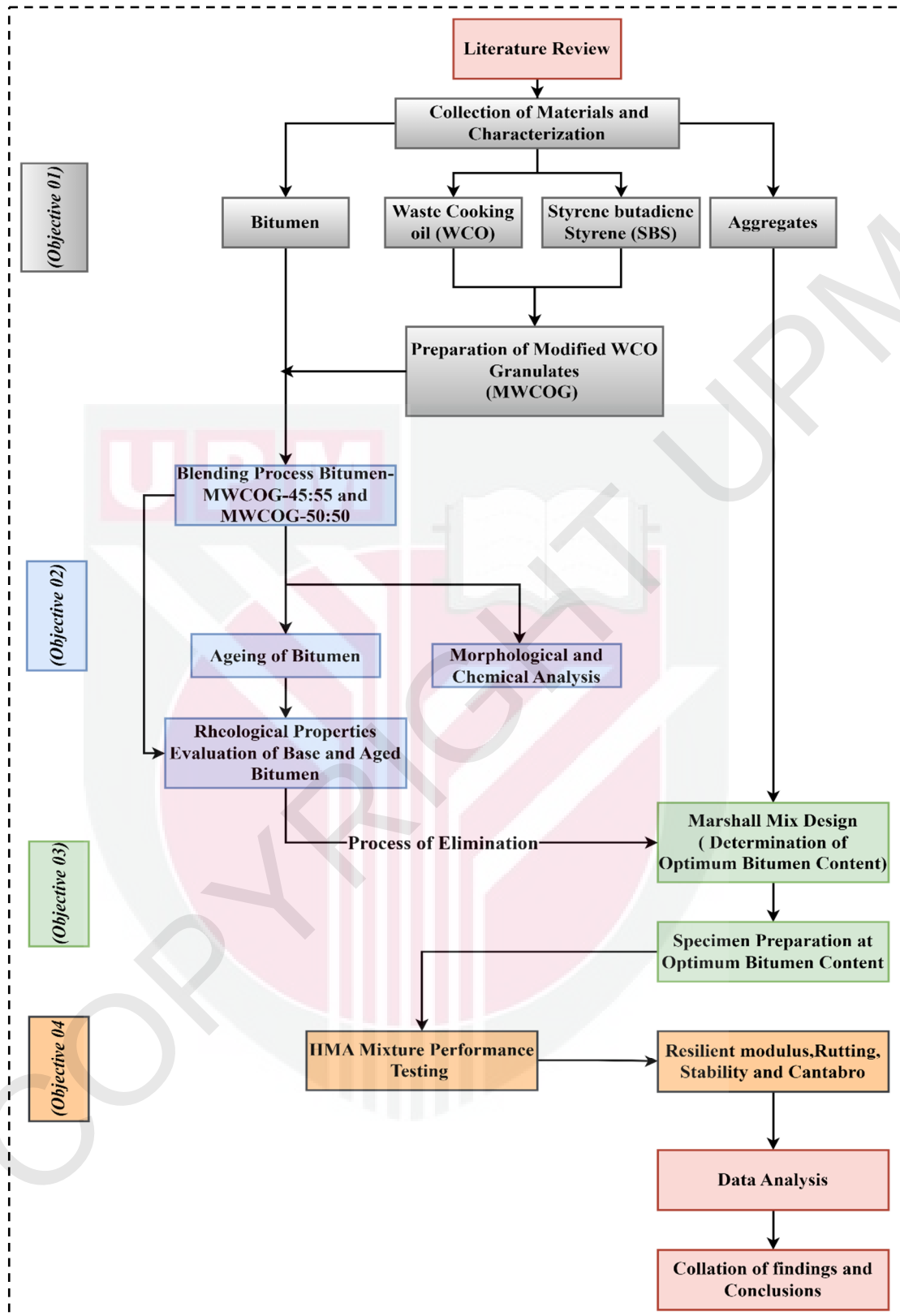


Figure 3.1: Flow chart of the study

3.2 Characterisation of Materials (Objective 1)

The primary objective of this section is to present each selected material for this study and to understand their compatibility within the context of the bitumen and asphalt mixtures as shown in a flow chart (Appendix C). The specific properties of the selected materials along with the origin and the background are also presented in this section. The prescribed standards of the ASTM and the AASHTO were used to test the bitumen, aggregates, waste cooking oil and the SBS. Furthermore, these properties were cross-referenced with standard specifications to ensure their suitability for the process of modifying bitumen and asphalt mixtures. The main focus of the study is to utilise the waste cooking oil and its effectiveness on the bitumen properties. Therefore, the WCO pre-modification is an important part of the study before its incorporation directly into bitumen. The subsequent section provides the detailed procedure used for the WCO modification. Furthermore, comprehensive morphological and chemical testing protocols have been carefully outlined to confirm the suitability of the materials within bitumen and asphalt mixtures.

3.2.1 Properties of bitumen

In this study, a 60/70 penetration grade bitumen sourced from Qastalani Sdn Bhd Malaysia was employed. The selected bitumen grade used in the study did not contain pre-added additives to ensure precise analysis, as the main research focus was on bitumen modification with the WCO. The description of the basic properties of the bitumen with specifications and the standard test protocols to determine the characteristics are provided in Table 3.1.

Table 3.1: Bitumen tests, standards and specifications

Material	Property Test	Specification	Standard
Bitumen 60/70	Penetration @ 25°C (dmm)	60-70	(ASTM D5, 2019)
	Softening point (°C)	48	(ASTM D36, 2008)
	Specific gravity	1.0	(ASTM D70, 2021)
	Brookfield Viscosity @ 135°C (Pa. s)	3.0 Pa.s	(ASTM D 4402, 2000)
	Ductility @ 10 °C (cm)	≥100	(ASTM D 113-07, 2002)
	Mass loss (%)	1.0 max	(ASTM D2872-22, 2022)
	Flash and Fire Test	250	(ASTM D92, 2007)
	Rutting Parameter (Unaged)	1.0 min	
	Rutting Parameter (RTFO-aged)	2.2 min	(ASTM 7175, 2001)
	Fatigue Parameter (PAV-aged)	5000 max	

3.2.2 Properties of aggregates

The asphalt mixture primarily consists of aggregates, accounting for more than 95% of its composition. Therefore, it is essential to place significant emphasis on the careful selection of aggregate types and quality, while also considering their cost-effectiveness. In Malaysia, various types of aggregates are available, but granite stands out as the predominant choice in the construction industry. This preference is attributed to its notable characteristics, including low abrasion and high strength. The granite aggregates were sourced from the Kajang Rocks Quarry Sdn Bhd. The basic properties of the granite aggregates were evaluated to make sure to comply with the standard specifications. The specification and the standard test methods are shown in Table 3.2.

Table 3.2: Aggregates standards, specifications, and tests

Material	Property Test	Specification	Standard
Granite aggregate	Los Angeles Abrasion	30 % max	(ASTM C131/C131M-14, 2014)
	Flakiness and Elongation	<20%	(ASTM 4791, 2019)
	Aggregate impact value	<15%	(ASTM D5874, 2016)
	Specific gravity and water absorption coarse	-	(ASTM C127, 2004)
	Specific gravity and water absorption fine	-	(ASTM C128, 2015)
	Soundness of aggregates (sodium sulphate)	12%	(ASTM C 88, 1999)

3.2.3 Properties of Styrene Butadiene Styrene

SBS is a member of the thermoplastic block copolymer family and possesses a biphasic morphology characterized by the presence of rigid polystyrene (PS) blocks connected by rubbery polybutadiene (PB) blocks. This unique structure allows SBS copolymers to exhibit a cross-linked elastomer network behaviour across a wide temperature range. The SBS with an S/B block ratio of 30/70 were procured from Qastalani Sdn Bhd Malaysia which is a common type of SBS for bitumen modification purposes. The properties related to the SBS are provided in the flow chart (Figure 3.2).



Figure 3.2: Styrene Butadiene Styrene (SBS)

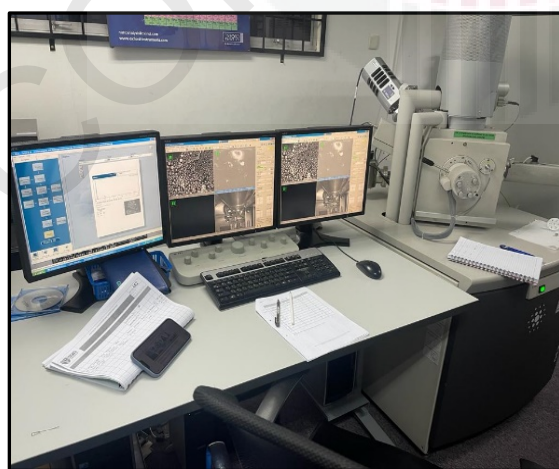
3.3 Properties of waste cooking oil

The raw waste cooking oil (WCO) was collected domestically near Universiti Putra Malaysia (UPM) Seri Kembangan Selangor. The collected raw WCO was pre-processed before the modification for the phase change into rubbery solid material. The modification and the pre-processing of the WCO and the standard testing procedures were given the utmost importance. Since the main focus of the study is the performance improvement of the modified bitumen and the asphalt mixtures which

mainly depends on the quality of the modified WCO. The raw WCO physical and chemical properties were determined for better description. The modified WCO surface structure and detail morphology were analysed with the FESEM while the chemical composition was determined with Energy Dispersive X-ray (EDX) and mapping function.

3.3.1 Structure and surface morphology of materials

Field Emission Scanning Electron Microscope (FESEM) is an important equipment that can be used to analyse the morphology and surface texture of the materials on a scale of micrometre to nanometer. Therefore, the FESEM model (FEI Nova Nano SEM 230) is used for analysis purposes with a maximum of 10 kV of voltage. The conductivity of the samples of the materials was improved by applying the thin film of platinum coating ($<10\mu\text{m}$) using a sputter at low vacuum. The samples without any coating cause the accumulation of unnecessary electrons on the surface of samples and usually cause the charging that can affect the morphological analysis of the material. Figure 3.3 depicts the platinum coating samples and analysis.



FESEM setup



Material with platinum coating

Figure 3.3: Morphological analysis of materials

3.3.2 Elemental analysis and chemical composition

The chemical composition of the materials was further evaluated using the EDX function of the FESEM. The specific area of the material was selected for the EDX and mapping to determine the elemental composition. The mapping with the EDX technique is necessary to observe and understand the behaviour of WCO in the modification process. The WCO chemical composition and the mapping would notably provide an interactive understanding of bitumen and asphalt mixtures. The image analysis and the chemical composition of materials were performed at the Institute of Nanoscience and Nanotechnology (ION2) at Universiti Putra Malaysia (UPM).

3.3.3 Pre-processing and modification of WCO

The pre-processing and modification of the raw WCO are necessary to overcome the deficiencies encountered in the previous studies. Incorporating a small quantity of less than 2wt.% of the WCO into the bitumen causes a sudden decrement in the performance of the modified bitumen. The raw WCO in this study was modified into a rubbery-solid state before being added to the bitumen for modification and to ensure the strong compatibility between the modifier and bitumen. The process of modification is done by dividing it into three phases. In the first phase, the collected raw WCO was simply filtered following the simple filtration process by using the filter paper with a pore size of 11 μm and thickness of 180 μm as shown in Figure 3.4a. After the filtration, the suspended impurities of the WCO remained on the filter paper and the residual WCO was collected for further modification. Second, the filtered

WCO was modified with the SBS at different ratios of SBS: WCO (Figure 3.4b). The proportions and the weightage of each ratio used are provided in Table 3.3.

Table 3.3: Modification proportion of SBS and WCO

Proportion	SBS weight (g)	WCO content (g)
20:80	60	240
30:70	90	210
40:60	120	180
45:55	135	165
50:50	150	150

The pre-swelling of SBS with various oils has been reported in studies to enhance the cross-linking of the SBS before utilisation for modification purposes (Luo et al., 2022a; Zhang et al., 2019). In this study the filtered WCO was modified by blending the SBS: WCO at 20:80, 30:70, 40:60, 45:55 and 50:50. The manual blended materials were heated in the oven at 160 °C temperature for 45 minutes. The oven-heated mixtures were stirred every 15 minutes for better homogeneity and well dissolvment of the SBS into the WCO. After blending and heating, the materials were allowed to cool at room temperature for 120 minutes, culminating in a rubber-solid state (Figure 3.4c). Lastly, the modified WCO mixtures were cut into long strips followed by small pieces of $\leq 3\text{mm}$ in size for the bitumen modification (Figure 3.4f). The prepared mixtures were named modified waste cooking oil granulates MWCOG.



WCO filtration



WCO and SBS



WCO and SBS after heating



Material after cooling



Modified material strips



Modified granulates

Figure 3.4: Steps involved in modification of WCO

3.4 Preparation process of modified bitumens (Blending)

In the preparation of modified bitumens, the modified waste cooking oil granulates (MWCOG) were added to bitumen by 5%, 10%, 15%, 20%, and 25% by weight of

base bitumen. A total of 50 modified bitumens were prepared, 05 for each ratio (20:80, 30:70, 40:60, 45:55 and 50:50). Firstly, the base bitumen was poured into a metal container and kept at 150 °C. The shear mixer model (RW20DZM) from IKA was used to prepare all the modified bitumens at 2000 rpm for 30 minutes at 150 °C $\pm$ 3 °C as shown in Figure 3.5. The MWCOG were added to the bitumen incrementally initially at 400 rpm and this procedure could reduce the time of blending and enhance the dissipation of granulates within the bitumen which leads to avoiding any bitumen ageing during the blending. After adding the required MWCOG, the shear mixer speed was increased to 2000 rpm for the dissolution of the granulates within the bitumen matrix to achieve a homogeneous blend. The names of modified bitumens with 5%, 10%, 15%, 20%, and 25% were coded in Table 3.4.



Figure 3.5: Blending process of MWCOG-bitumen

Table 3.4: Studied bitumen description

Material	Sample coding	Modified WCO granulates wt. (%)
Base bitumen	Base	0
MWCOG-20:80	20:80-5%	5
	20:80-10%	10
	20:80-15%	15
	20:80-20%	20
	20:80-25%	25
MWCOG-30:70	30:70-5%	5
	30:70-10%	10
	30:70-15%	15
	30:70-20%	20
	30:70-25%	25
MWCOG-40:60	40:60-5%	5
	40:60-10%	10
	40:60-15%	15
	40:60-20%	20
	40:60-25%	25
MWCOG-45:55	45:55-5%	5
	45:55-10%	10
	45:55-15%	15
	45:55-20%	20
	45:55-25%	25
MWCOG-50:50	50:50-5%	5
	50:50-10%	10
	50:50-15%	15
	50:50-20%	20
	50:50-25%	25

3.5 Identification of optimal MWCOG ratio

The study involved blending the modified waste cooking oil granulates (MWCOG) with base bitumen at various ratios, specifically 20:80, 30:70, 40:60, 45:55, and 50:50, with concentrations of 5%, 10%, 15%, 20%, and 25% by weight. These blended modified bitumens underwent testing for rotational viscosity and rutting parameters at different temperatures. Each tested bitumen underwent a comprehensive analysis to assess its suitability for further evaluation. The study determined the mixing and compaction temperatures and identified the performance grade of the modified bitumen to identify the best-performing blends.

3.6 Characterization of WCO modified bitumen (Objective 2)

The base and the WCO modified bitumen characterization are significant aspects of the interaction understanding of the bitumen and added additives. The rotational viscosity, rheological properties, and morphological and chemical analysis of the bitumen and the WCO modified bitumen were performed and explained in a flow chart (Appendix C). The tasks were accomplished by blending various ratios of modified WCO with the base bitumen. Additionally, 10 modified bitumen blends were prepared by incorporating two modified WCO ratios (45:55 and 50:50). These blends underwent short-term (RTFO) and long-term (PAV) ageing. After ageing, the modified blends were subjected to a series of tests, including rotational viscosity, dynamic rheological, morphological, and chemical analyses. This section outlines the work carried out in alignment with Objective 02 and provides details on the laboratory procedures employed.

3.6.1 Ageing of base and modified bitumen

Ageing of the bitumen is the primary phenomenon that mainly occurs due to the oxidation and loss of the volatile components. The initial ageing occurs during the hot mix asphalt production due to the oxidation and volatilization called short-term ageing. However, the ageing that occurs during the service life of the pavement may happen due to the progressive oxidation is called long-term ageing. The WCO modified bitumen was short-term and long-term aged to simulate the field behaviour and characterized under various schemes of bitumen testing.

3.6.1.1 Rolling Thin Film Oven (RTFO)

The short-term ageing of the WCO-modified bitumen was achieved by subjecting the samples to heat and air using the Rolling Thin Film Oven test (RTFO) following the guidelines outlined in (ASTM D2872-22, 2022). The short-term ageing of the modified bitumen involved placing 35 grams of the specified bitumen into the standard bottles used for the RTFO test. These bottles filled with bitumen were then exposed to 4000 ml/min of airflow and a temperature of 163°C for approximately 85 minutes, as illustrated in Figure 3.6. After completing the test, the weight loss of the samples was measured, and the aged bitumen was subsequently stored in an airtight container at room temperature for further testing and analysis.



Figure 3.6: Short-term ageing of base and modified bitumen using RTFO

3.6.1.2 Pressure Age Vessel (PAV)

The accelerated ageing and oxidation by applying the pressurized air and the heat to simulate the long-term service life of bitumen is referred to as PAV. This test procedure only aims to simulate the modifications in the rheological properties of the

bitumen during the long-term service life. Whereas the simulation does not need to be as accurate as the field environment. The test was performed following the (ASTM D6521, 2019) and (ASTM D2872-22, 2022). During this test, preheated bitumen with the appropriate fluidity was poured into the conditioned pans, each containing approximately 50 grams of bitumen, and subsequently positioned within the pan holder (Figure 3.8). The pan holder, along with the prepared pans with bitumen was slotted into the preheated Pressure Aging Vessel (PAV) and sealed securely. The temperature within the PAV vessel was conditioned to 100°C, and it was pressurized and maintained at 300 psi for a duration of 20 hours in accordance with the SHRP (Strategic Highway Research Program) specifications. Following the 20-hour testing time, the pans were removed from the vessel by gradually releasing the high pressure within the PAV vessel. The long-term aged samples from each pan were consolidated into a single container and placed in a vacuum chamber to eliminate any entrapped air and bubbles before proceeding with additional testing (Figure 3.7).



Figure 3.7: PAV and vacuum chamber for bitumen long-term ageing

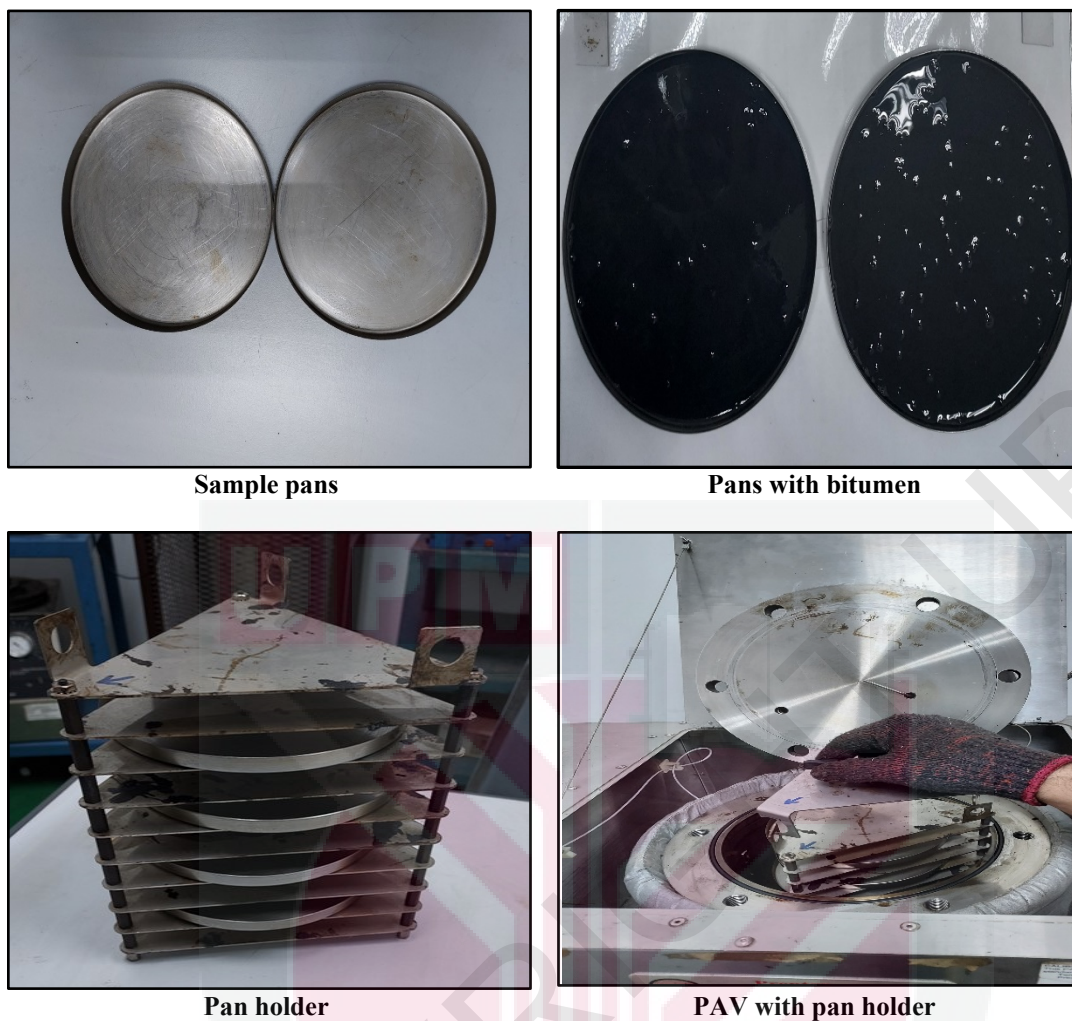


Figure 3.8: Steps involved in PAV test

3.7 Rotational viscosity

The rotational viscosity test determines the flow behaviour of the bitumen to provide certain assertiveness that the bitumen can be pumped and handled during the hot mixing of the mixtures. This study determined the rotational viscosity of the modified waste cooking oil bitumens using the Brookfield viscometer (Model DV-II, Brookfield Engineering Inc., USA) as per ASTM D4402. The Rotational viscometer (RV) is used to determine the viscosity of the bitumen (Figure 3.9). The RV works by measuring the torque required for keeping a cylindrical spindle rotating at a constant speed while

submerged in a sample of bitumen held at a constant temperature. The viscosities of all 10 modified bitumens were measured at a temperature of 90 °C, 105 °C, 120 °C, 135 °C, and 165 °C with spindle #27 and 20 rpm. A replicate of three for each bitumen containing different percentages of MWCOG was prepared and tested for RV.



Figure 3.9: Rotational viscometer

Thereafter, the mixing and the compaction temperature were determined at specified temperatures of 135 °C and 165 °C) by plotting the viscosity-temperature relationship. The desired temperature was determined from the viscosity-temperature relationship of asphalt binder at 0.17 ± 0.02 Pa s and 0.28 ± 0.03 Pa s. Moreover, the ageing indices of the WCO modified bitumen were also determined. The RTFO aged bitumen values of the RV tests were utilized for the ageing index (A.I).

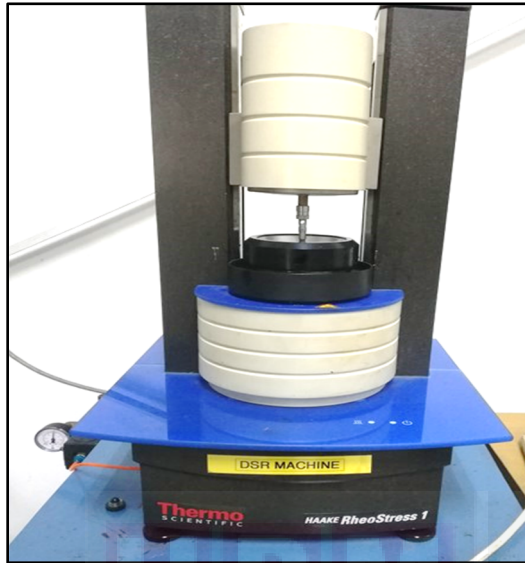
$$A.I \text{ of } RV = \frac{RV_{aged \text{ test value}}}{RV_{unaged \text{ test value}}} \quad (3.1)$$

3.8 Dynamic rheological properties of bitumen

The WCO modified bitumen (MWCOG-45:55 and MWCOG-50:50) was characterized by its viscoelastic properties employing the dynamic shear rheometer (DSR) at intermediate and high temperatures. The DSR model Haake RheoStress 1 (Thermo Scientific) was used to determine the rheological characteristics in accordance with the (ASTM 7175, 2001) or AASHTO T315. The DSR evaluates the rheological properties of bitumen by measuring the complex shear modulus (G^*) and phase angle (δ) at a specified temperature and loading frequency. The G^* of the bitumen corresponds to the resistance of the bitumen towards the oscillating deformation, while the δ reflects the lag between shear stress and shear strain.

3.8.1 DSR testing procedure

The viscoelastic characteristics of the WCO modified and the base bitumen were determined by placing the bitumen thin specimen between the DSR oscillation spindle and the lower fix plate by following the (ASTM 7175, 2001). A 25mm diameter parallel plate geometry with a 1mm gap and an 8mm diameter geometry with a 2mm gap were used for the higher temperature (40–82°C) and intermediate temperatures (10–40°C) respectively. The testing was conducted under sinusoidal loading as illustrated in Figure 3.10.



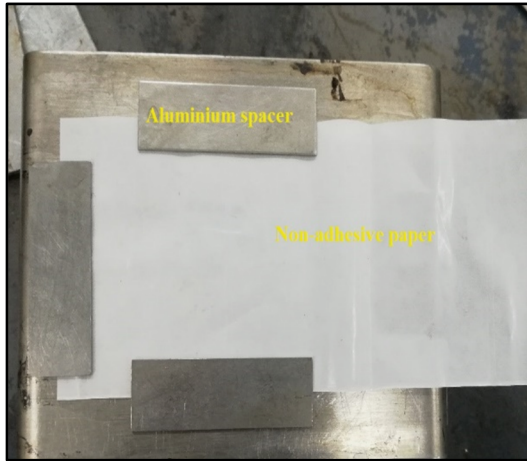
DSR



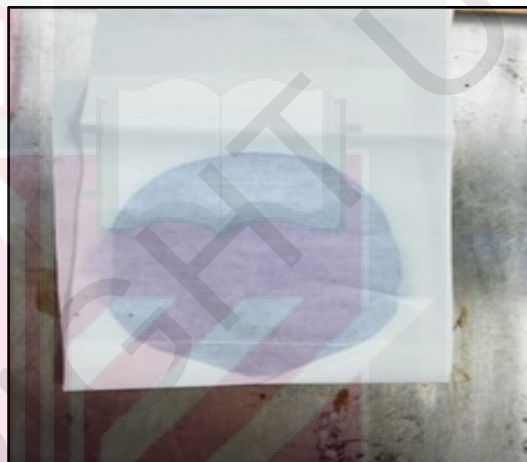
25 mm and 8 mm spindle

Figure 3.10: Dynamic shear rheometer

For sample preparation, the hot pour method was employed. In this method, a well-stirred and homogeneous bitumen sample was poured onto a non-adhesive sheet. The non-adhesive sheet was adjusted with 1mm and/or 2mm gaps, depending on the specific sample requirements, using aluminium spacers. Another sheet was placed on top of the sample, and clamps were applied to compress the bitumen sample to achieve the desired standard sample thickness. Once the bitumen sample had cooled to ambient temperature, it was cored to the required diameter using the coring tool provided by the DSR machine, as depicted in Figure 3.11.



DSR sample preparation



Clamping and cooling of sample



Cutting of sample

Figure 3.11: Steps involved in the preparation of DSR sample

3.8.2 Temperature sweep

The WCO-modified bitumen specimens were examined for temperature effects both before and after the ageing processes, including short-term ageing (RTFO) and long-term ageing (PAV). These evaluations were conducted using an oscillation test with a temperature sweep test (TST). The TST was carried out at higher temperatures (40–82 °C) and intermediate temperatures (10–40 °C), maintaining a constant frequency of 1.59 Hz and a consistent 6 °C temperature interval. The testing procedure was performed in controlled stress (CS) mode, with loading conditions of 120 Pa, 220 Pa, and 50 kPa for the unaged, short-term aged, and long-term aged specimens, respectively.

3.8.2.1 Rutting and fatigue parameter

The base bitumen and WCO-modified bitumens in two different ratios, specifically MWCOG-45:55 and MWCOG-50:50, were subjected to testing to determine their failure temperatures across a range of testing temperatures, as outlined in section 3.8.2. The rheological parameters, complex modulus (G^*) and phase angle (δ), which were measured during the temperature sweep test, were subsequently utilized to calculate the rutting parameter ($G^*/\sin \delta$). This parameter, in turn, was employed to ascertain the failure temperatures of the modified bitumen. Conversely, the bitumen was subjected to RTFO ageing followed by PAV ageing in order to assess the fatigue parameter ($G^* \cdot \sin \delta$) of the modified bitumens. As per the Superpave specifications, the $G^*/\sin \delta$ for the unaged bitumen must be higher than 1000 Pa to control the field rutting while the maximum limit for the RTFO aged bitumen is 2200 Pa (Kennedy et

al., 1994). Nonetheless, it's important to note that the $G^* \cdot \sin \delta$ value for PAV-aged bitumen should not exceed 5000 kPa. This value is indicative of the bitumen's ability to resist cracking at intermediate temperatures.

3.8.2.2 Isochronal plots

During dynamic rheological testing under a temperature sweep setup, the graphical representation of the complex modulus and phase angle as a function of temperature is referred to as an isochronal plot. This data was obtained by maintaining a constant frequency while varying the temperatures. The data obtained from rheological testing of unaged and short-term aged WCO modified bitumen was employed to create isochronal plots. These plots provide a better understanding of the behaviour of the modified bitumen across different temperature ranges at a constant frequency.

3.8.3 Frequency sweep

Dynamic rheological testing under varying temperature and frequency ranges is referred to as frequency sweep test (FST). In this, FST was conducted at a temperature range of 35 °C to 85 °C and frequency of 0.1 to 14 Hz in linear viscoelastic range (LVE) of bitumen. The controlled strain mode of testing was opted by following the (ASTM 7175, 2001). The data points obtained from the FST were further treated to evaluate the behaviour of the WCO-modified bitumens. Furthermore, the Black space diagram, the master curve at a reference temperature of 65 and the Cole-Cole diagram was developed to analyse the insight behaviour of the WCO-modified bitumen before and after short-term ageing.

3.8.3.1 Black space and Cole-Cole diagram

The dynamic rheological data obtained under the FST test scheme were used to produce the Black space and the Cole-Cole diagrams. These plots allow to observe the dynamic rheological behaviour of bitumen in one plot by eliminating the temperature and the frequency. Therefore, the time-temperature superposition principle is not necessary to be performed on the raw data obtained for this representation. The interpretation of complex modulus and the phase angle on a single plot is called a Black space diagram. The smooth curves of the black space diagram are the effective indication of temperature and time equivalency whereas the disperse curves depict the TTSP breakdown. These breakdowns are usually due to the adoption of high polymers, or the presence of high wax and asphaltene content. In contrast, the Cole-Cole diagram is a graphical representation of the storage and viscous modulus components, typically reflecting the stiffness of bitumen. This diagram is created by plotting the storage and loss modulus, with the 45° line serving as a divider, indicating the viscous and elastic properties of the bitumen.

3.8.3.2 Master curve -WLF equation

The practical interpretation of the FST data at reference temperatures is called the master curve. This approach facilitates the continuing generation of rheological parameters by adjusting complex modulus data from different temperatures to a reference temperature. The acquired FST data at various temperature ranges require to be shifted at one reference temperature by employing the TTSP. However, this shifting of the data for the master curve generation mainly depends on the shift factors. The

shift factors have been computed using the Williams – Landel – Ferry (WLF) model (Williams et al., 1955). The WLF equation utilized to calculate the shift factors for the angular reduced frequency is expressed below in Equation 3.2.

$$\log \alpha_T = \frac{C_1(T - T_0)}{C_2 + (T - T_0)} \quad (3.2)$$

Where shift factors are represented by α_T , FST temperature is denoted as T , and the T_0 represents the reference temperature (65 °C), and the empirical constant C_1 and C_2 .

3.8.3.3 Sigmoidal model - rheological Modelling

The sigmoidal model was introduced by the National Cooperative Highway Research Program (NCHRP) in the Mechanistic-Empirical Pavement Design Guide (ME PDG) for the computation of the dynamic modulus. In the ME PDG, the Sigmoidal Model is employed to describe the rate dependence of the modulus master curve. After the determination of the shift factor using the WLF equation, the sigmoidal model was used for the experimental data modelling and explained in Equation 3.3. The smooth master curves were developed at a reference temperature of 65 °C using the complex modulus at all temperature ranges. The MS Excel solver function was used to fit the data.

$$\log |G^*| = v + \frac{\alpha}{1 + e^{(\beta + \gamma \log f_r)}} \quad (3.3)$$

Where the lower asymptote position of the curve is represented as v , the reduced frequency as $\log f_r$, the difference between the values of upper and lower asymptotes by α , and the shape of the curve between the asymptotes is related to β and γ .

3.9 Separation index of modified bitumen

The storage stability of the modified bitumens is an important technical parameter of production at higher temperatures. The tendency of the separation of modified bitumen was determined by the aluminium tube test following the ASTM D7173. First, the modified bitumen with MWCOG-45:55 and MWCOG-50:55 was poured into the aluminium tube of standard size. Then, the tubes were sealed carefully and placed in the oven for 48 ± 1 h at 163 ± 5 °C. Subsequently, the tubes were placed in a freezer for about 4 h at -10 °C to solidify the bitumen. Afterwards, the prepared samples were cut into three equal parts, and the top and bottom parts of the tubes were tested for complex shear modulus and the middle portion was discarded. The evaluation of the rheological parameters for the modified bitumen's storage stability seems more reliable than the conventional softening point and penetration tests (Goli et al., 2017; Yun et al., 2022). Hence the separation index (SI) based on the complex modulus results was proposed by SHRP and expressed as.

$$\text{Separation Index (SI)} = \frac{G^*_{(\text{Top})}}{G^*_{(\text{Bottom})}} \quad (3.4)$$



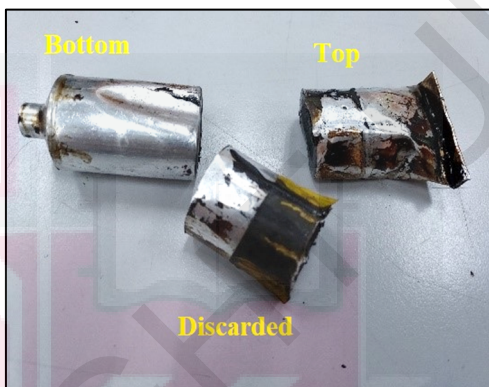
Aluminium test



Tubes with modified bitumen



Cutting of tube



Discarded and used portions of tubes

Figure 3.12: Process of storage stability test

3.10 FTIR analysis of bitumen

FTIR spectroscopy was conducted by employing a 400 PerkinElmer spectrometer for the functional group assessment. The predictable chemical reactions and modification mechanism were investigated in the wavelength range of 650 to 4000 cm^{-1} with 32 successive scans at 4 cm^{-1} . The base and modified bitumen spectra were obtained using the Attenuated Total Reflection method. The FTIR analysis was performed at the Material Characterization Laboratory (MCL), Department of Chemical Engineering, Universiti Putra Malaysia (UPM). The assessment of the change in the peaks of the FTIR spectra of the modified bitumen was also compared with the base materials (Bitumen, WCO, SBS) spectra.

3.11 Process of elimination for blend selection

In the previous section, the 10 WCO modified and the base bitumen i.e., base, 45-55-5%, 45-55-10%, 45-55-15%, 45-55-20%, 45-55-25% and 50-50-5%, 50-50-10%, 50-50-15%, 50-50-20%, 50-50-25%, were evaluated for the rheological, morphological and the chemical analysis. However, the blends with promising performance were further characterized for the evaluation of the mechanical performance.

3.12 Marshall mix design (Objective 3)

The selected WCO modified and base bitumen in the previous section were further characterized after the process of elimination by following the Marshall mix design (ASTM D6926, 2016). The AC14 dense-graded asphalt mixture was produced on a laboratory scale. The evaluation of the economical asphalt mixture within the specification is an important task in the Marshall mix design. The mixture design's main task is the determination of the optimum bitumen content (OBC). The pavement performance, durability and long service life mainly depend on the OBC and specified gradation of the aggregates. The materials used in preparing the cylindrical Marshall specimen were tested to make sure they met the necessary specifications. The specific tasks involved in determining the OBC and the total number of prepared asphalt mixtures are outlined in a flow chart (Appendix C).

3.12.1 Aggregate gradation

In the Marshall mix design process, the Hot Mix Asphalt (HMA) AC14 gradation specified by JKR (Jabatan Kerja Raya) specifications was employed. In this research,

granite aggregates were selected due to their widespread availability and abundance, along with their compatibility with JKR criteria. Furthermore, the fine material left in the pan, referred to as granite powder, was utilized as a filler in the asphalt mixture. The specifics of the AC14 gradation, including the aggregate size and passing percentages applied in this study, are presented in Table 3.5.

Table 3.5: AC14 HMA gradation specifications

Sieve (mm)	Passing (%)		
	Upper limit	Medium limit	Lower limit
20	100	100	100
14	90	95	100
10	76	81	86
5	50	56	62
3.35	40	47	54
1.18	18	26	34
0.425	12	18	24
0.150	6	10	14
0.075	4	6	100
Pan (Filler)			

3.12.2 Marshall cylindrical specimens preparation

The cylindrical specimens were prepared following the Marshall mix design (ASTM D6926, 2016) and (D1559, 1989) to evaluate the optimum bitumen content. The seven modified bitumen blends including the base i.e., Control, 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15%, were opted for the asphalt mixture design the OBC. The 15 cylindrical specimens were prepared for each mix design at varying content of bitumen (4.0 to 6.0%) with 0.5% increment. A set of three specimens was prepared for each bitumen content to ensure accuracy. The total weight of the cylindrical specimens, including aggregates and filler, was maintained at 1150 g. A 6% filler content was employed following the AC14 gradation. However, the air voids were maintained at 4% to simulate the field condition for the determination of

the OBC following the specification. The mixing and the compaction temperatures for the asphalt mixture were determined from the temperature-viscosity relationship for the WCO and base-modified bitumen and are detailed in the previous Objective of the study. The Marshall compactor was used for the compaction and the preparation of the cylindrical specimens (101.6 mm and 63.4 mm). The 75 blows on each side of the specimens were applied to achieve the desired thickness and the 4% voids as illustrated in Figure 3.13. A total of 140 cylindrical specimens were prepared for the 7 mixture designs to determine the OBC. The 105 were compacted as cylindrical specimens while the remaining 35 loose samples were utilized for the theoretical maximum density (TMD) which is detailed in a subsequent section. The compacted specimens were assessed for their density and volumetric characteristics. Moreover, the specimens underwent testing for Marshall stability, flow, and stiffness modulus. The density, volumetric properties, stability, and resilient modulus data were plotted versus the varying bitumen content to determine the OBC. The Asphalt Institute method was employed to determine the OBC by taking the average values of 4% air voids, Maximum density and stability.



Figure 3.13: Cylindrical compacted specimens

3.12.3 Determination of asphalt mixture's volumetric properties

The volumetric properties of cylindrical specimens were determined at each varying content of the bitumen. These properties have a significant impact on the asphalt mixture's performance. The associated volumetric properties of asphalt mixtures are as follows.

- a Theoretical maximum density (G_{mm})
- b Bulk specific gravity (G_{mb})
- c Voids in total mix (VTM)
- d Voids in mineral aggregates (VMA)
- e Void filled with bitumen (VFB)

The loose specimens of asphalt mixtures of control and the WCO modified asphalt mixtures were used for the determination of the theoretical density in accordance with (D2041, 2019) and the Rice method. The mixture aggregates were separated from each other carefully without tampering with the texture or the original size. The separated mixture was placed in the vacuum container and submerged in water at a temperature of 25 °C. A vacuum pressure of 4 kPa or 30 mm Hg was applied for a duration of 15 ± 2 minutes. During this process, continuous agitation using a vibrator was employed to help remove any entrapped air from the specimens. Finally, the vacuum pressure was gradually released, and the weight of the container along with the sample was measured. This measurement was necessary to calculate the specific volume of the asphalt mixture. The TMD can be computed as follows:

$$G_{mm} = \frac{A}{A - (C - B)} \quad (3.5)$$

where,

G_{mm} = theoretical maximum density

A = dry mass in air, g

B = mass of container in water, g

C = container and specimen mass in water, g

Another important volumetric parameter is the bulk specific gravity sometimes also stated as the actual specific gravity. It varies in comparison to the TMD as it primarily considers the presence of air voids within the compacted specimen. The bulk specific gravity was computed by utilizing the compacted specimen in accordance with (D2726, 2002). The cooled specimen's dry weight, weight in water and saturated weight were taken to calculate the specific gravity as follows:

$$G_{mb} = \frac{A}{B - C} \quad (3.6)$$

where,

G_{mb} = bulk-specific gravity

A = dry mass of compacted specimen in air, g

B = surface saturated dry weight of compacted specimen, g

C = compacted specimen mass in water, g

The bulk specific gravity and the TMD can be utilized to compute the void in total mix (VTM) following the equation below.

$$VTM\% = \frac{G_{mm} - G_{mb}}{G_{mm}} \times 100 \quad (3.7)$$

where,

VTM % = voids in total mix

G_{mb} = bulk-specific gravity

G_{mm} = theoretical maximum density

The compacted asphalt mixture usually comprises intergranular voids which mainly contain the effective bitumen and air voids (Roberts et al., 1996).

The low voids in mineral aggregates (VMA) resist aggregate from bitumen coating whereas the high VMA corresponds to lower stability. It can be computed as follows

$$VMA \% = 100 \times \left(1 - \frac{G_{mb}(1 - P_b)}{G_{sb}} \right) \quad (3.8)$$

where

VMA % = percentage voids in mineral aggregates

G_{mb} = bulk-specific gravity

P_b = content of bitumen by weight of a mixture

G_{sb} = bulk specific gravity of aggregate

The percentage volume of the VMA that is filled with the bitumen is called the volume filled with the bitumen (VFB) and is represented as:

$$VFB \% = 100 \times \frac{VMA - VTM}{VMA} \quad (3.9)$$

3.12.4 Marshall Stability and Flow

The mix design cylindrical specimen of seven asphalt mixtures was experimentally assessed for Marshall stability and flow (D1559, 1989). It exhibits the performance of the asphalt mixtures by evaluating the maximum endured load. The ability of the cylindrical specimen to uphold its maximum load at a strain rate of 50.8 mm/min is referred to as stability. Moreover, the horizontal resistance of the specimens against the vertical axis loading is called flow or the plastic flow of the specimen. The low stability and the higher flow rate of the asphalt mixtures are not acceptable as they cause earlier pavement failure under normal conditions (Roberts et al., 1996). The cylindrical compacted samples of all seven mix designs were tested for the Marshall stability and flow. A total of 105 specimens were conditioned in a water bath for 30 minutes at 60 °C prior to the final testing. The compacted specimens' thickness did not adhere to the prescribed procedure of 63.5 mm. As a result, the sustained load or stability of the specimens cannot be accurately determined. Therefore, the obtained stability results were harmonised by multiplying it with the correction factor. The corrected values were further utilized for the determination of the optimum bitumen content following the Marshall mix design. Figure 3.14 depicted the testing procedure of specimens.



Specimens conditioning



Stability and flow testing

Figure 3.14: Marshall stability setup

3.12.5 Resilient modulus (M_R)

The asphalt mixture stiffness performance is usually assessed by the resilient modulus (M_R) test. The cylindrical specimens of base and WCO modified asphalt in this study were tested for M_R in accordance with (D4123, 2001). The asphalt cylindrical specimens were tested using the material testing apparatus (MATTA). The 105 specimens at varying bitumen content of all WCO-modified asphalt mixtures were used to evaluate the resilient modulus under repeated cyclic loading. All specimens were placed under the conditioning chamber at 25 °C prior to the testing conditions. A repeated load of 1200 N in the form of a haversine waveform was applied to the cylindrical specimens along their vertical diametrical plane. Each specimen underwent five repeated pulses applied at a zero-angle position, and the test was subsequently repeated with the specimen rotated by 90° to verify the accuracy of the obtained results. The test parameters set for the testing are presented in Table 3.6. The vertical and horizontal displacement of the testing specimens were measured using the linear variable differential transformations (LVDTs) as illustrated in Figure 3.15. The

following equation has been used for the determination of the resilient modulus by assuming the Poisson ratio of 0.35 as per the JKR specifications (JKR, 2008).

$$M_R = \frac{P(v + 0.27)}{Dt} \quad (3.10)$$

where,

P = vertical applied load in N

V = Poisson ratio

D = horizontal deformation (mm)

t = thickness of the specimen (mm)

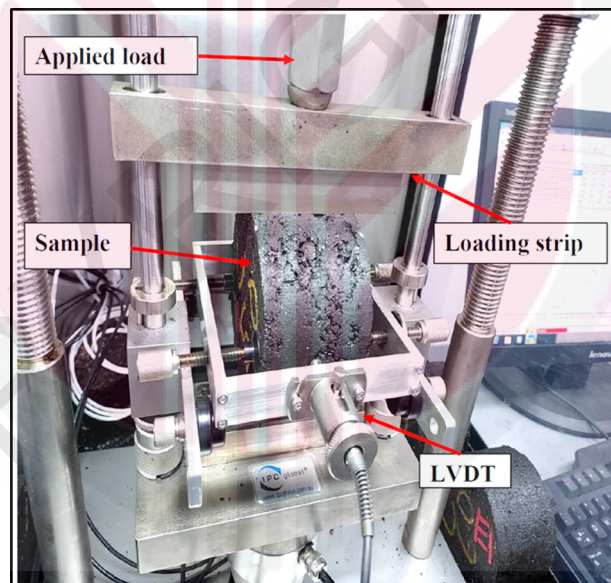


Figure 3.15: Test set up resilient modulus

Table 3.6: Resilient modulus test setup parameters

Setup parameters	Values
Temperature °C	25, 40
Loading pulse width (ms)	250
Pulse repetition period (ms)	3000
Pulse count	5
Poisson ratio	0.35
Peak loading force	1200

3.12.6 Selection of optimum bitumen content (OBC)

The data obtained from the prerequisite test parameters and analysis were plotted against the varying content of bitumen. The Asphalt Institute method was used to determine the OBC of asphalt mixtures. The average of the Marshall stability, air voids at 4%, maximum density and the resilient modulus was used to compute the OBC.

3.13 Performance analysis of mixtures (Objective 04)

This section of the study further characterises the effect of the WCO modified bitumens on the mechanical performance of the asphalt mixtures. After the OBC determination of the seven asphalt mixtures i.e., Control, 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15%. The 84 more cylindrical specimens were compacted specifically at the determined OBC to characterize their mechanical performances. The methodology and specimen preparation procedures for testing were also elaborated in detail. The performed test and total specimens in Objective 4 of the study are illustrated in a flow chart (Appendix C).

3.13.1 Dynamic creep/rutting test

The permanent deformation or rutting of the asphalt mixtures can be determined by the dynamic creep test. The 21 cylindrical specimens from the seven asphalt mixtures, each prepared at the Optimum Bitumen Content (OBC), were subjected to dynamic creep testing. The Marshall specimens were prepared to an average thickness of 63.5 mm and a diameter of 101.3 mm while maintaining an air void content in the range of 3% to 5%.

For each mixture type, triplicate specimens were tested to ensure the accuracy and reliability of the data following (EN-12697-25, 2012). Conversely, the cylindrical specimens were trimmed using a blade cutter on a diametrical axis from both faces of the specimen at least 50 mm in height prior to actual testing procedures as illustrated in Figure 3.16. The cutting process is performed to create a smooth testing surface, thereby preventing any unwanted friction between the specimen surface and the loading plate. The trimmed surfaces were further smoothened by scrubbing with the sandpaper and at last, the graphite powder layer was applied on both faces. The specimens were wrapped in aluminium foil to reduce the friction some more during the specimen testing as depicted in Figure 3.17. The prepared cylindrical specimens were placed in the conditioning chamber for 2 hours at 40 °C prior to the actual testing conditions. The specimens were then subjected to a cyclic axial load of 300 kPa. The loading conditions and the temperature set for the testing were selected as per the JKR-specified recommendations (JKR, 2008). The deformation resulting from the axial loading cycles, which ranged from 0 to 3600, was measured using LVDTs. Plots depicting strain (%) and vertical displacement (mm) versus cycles were generated. Furthermore, the specimens were preloaded with a 150 kPa load for approximately 1 minute to confirm the accurate positioning of the specimen and testing plate. Table 3.7 provides the other used parameters of the test.



Figure 3.16: Trimmed Marshall specimen for dynamic creep test

Table 3.7: Dynamic creep test setup parameters

Testing parameters	Values
Temperature °C	40
Cyclic loading stress (kPa)	300
Seating stress (kPa)	10
Cycle duration (ms)	200
Cycle repetition time (ms)	2000
Preload stress	150
Preload time (s)	60
Termination strain (%)	10
Termination cycle count	3600
Confine stress (kPa)	100

The equation below calculates the cumulative axial strain after n cycles and the load.

$$\epsilon_n = 100 \left(\frac{h_o - h_n}{h_o} \right) \quad (3.11)$$

where

ϵ_n = cumulative strain %

n = number of load cycles

h_o = average height (mm)

h_n = average height after n cycles of load

The creep rate (f_o) in micro-strain per loading cycle and the creep modulus for the particular period of loads are computed by the following equations:

$$f_o = \frac{\varepsilon_{n1} - \varepsilon_{n2}}{n_1 - n_2} \quad (3.12)$$

where,

ε_{n1} , ε_{n2} are the cumulative strains after loading of n_1 and n_2 in micro strains whereas the n_1 and n_2 are the specified time.

The creep modulus (E_n) after n loading cycles can be represented in MPa as.

$$E_n = \frac{\sigma}{\varepsilon_n} \times 1000 \quad (3.13)$$

Where σ is the stress applied in kPa and ε_n is the cumulative strain after n cycles in %.



Specimen graphite coating



Aluminium wrapping



Testing setup

Figure 3.17: Rutting test setup

3.13.2 Cantabro test

The asphalt mixture's durability, resistance to disintegration and cohesion loss can be determined by the Cantabro test. The durability of the dense graded asphalt mixtures is an important factor in the long service life of flexible pavements. A practical and

feasible testing method is necessary to assess these concern properties. Therefore, the Cantabro test shows the promise evaluation to meet these requirements. The 21 cylindrical specimens from the seven asphalt mixtures, each prepared at the OBC, were tested for the Cantabro test to determine the cohesion or stone loss. The Marshall specimens were prepared to an average thickness of 63.5 mm and a diameter of 101.3 mm. For each mixture type, triplicate specimens were tested to ensure the accuracy and reliability of the data following (ASTM C-131) and JKR specifications.

The prepared cylindrical samples were kept at ambient temperature and conditioned at 25 °C for six hours before the actual testing. The set of triplicates of each asphalt mixture was tested separately. The weight of the samples was measured before putting them in the Los Angeles drum. The Los Angeles machine was turned with a velocity of 188 to 208 rad/s for 300 revolutions without putting any balls inside the machine drum. After the completion of the required revolutions, the samples were taken out and weighed immediately for any loss. The loss of the sample after the testing should not be more than 15%. The following equation has been used for the determination of the average stone loss.

$$L = \frac{M_0 - M_1}{M_0} \times 100 \quad (3.14)$$

where

L = average loss of stones %

M₀ = Weight of sample before test

M₁ = Weight of sample after test



(a)



(b)

Figure 3.18: Cantabro test specimens: (a) before test (b) after test

3.14 Statistical analysis

The two-way analysis of variance (ANOVA), followed by post hoc analysis, was adopted in this study to statistically analyze the effect of modified waste cooking oil granulates (MWCOG) at various concentrations (45:55 and 50:50) on the properties of bitumen and asphalt mixtures. IBM SPSS Statistics was used to perform the analysis at a significance level of $\alpha = 0.05$. The two-way ANOVA was utilized to examine the impact of two independent variables (MWCOG concentration and blend type) on the dependent variables. This method assesses whether there are significant differences in the means of the dependent variables across different levels of each factor. The bitumen properties analyzed include, viscosity, and dynamic rheological properties,

while the asphalt mixtures were evaluated based on Marshall stability and resilient modulus. The independent variables are blend type (MWCOG-45:55 and MWCOG-50:50) and the varying percentages of MWCOG. It is important to note that the study is limited by the small sample size, with only three replicates for each percentage of MWCOG. While three replicates are generally accepted and practiced in engineering laboratory work due to the time and cost associated with sample preparation and testing, this small sample size may reduce the statistical power of the analysis and limit the ability to detect smaller effect sizes. This limitation may affect the robustness of the results, as a larger sample size is generally recommended to improve the reliability of statistical conclusions. Future studies should consider increasing the number of replicates to enhance the validity and generalizability of the findings. The following hypotheses were formulated:

- Null hypothesis: There are no significant main effects of MWCOG concentration and blend type on the properties of bitumen and asphalt mixtures.
- Alternate hypothesis: There are significant main effects of MWCOG concentration and blend type on the properties of bitumen and asphalt mixtures.

After conducting the two-way ANOVA to assess the effects of MWCOG concentration and blend type, a post hoc analysis was performed using Tukey's honestly significant difference (HSD) test to identify pairwise differences between factor levels. The post hoc analysis provided further statistical evidence beyond the ANOVA, enabling a more detailed interpretation of the specific factor levels that had a significant impact.

3.15 Summary

This chapter extensively outlines the methodology employed in both material preparation and data analysis for this study. Initially, the materials underwent thorough characterization to ensure their suitability for the research, adhering to standard specifications. The primary focus was the transformation of Waste Cooking Oil (WCO) from a liquid to a rubbery state. Detailed procedures for the pre-modification of WCO are elucidated. Subsequently, various modification ratios of WCO: SBS were blended with bitumen to identify the most promising modified blends. These selected blends underwent further characterization, involving rheological, morphological, and chemical analyses, with each method thoroughly detailed in this Chapter. Following a systematic elimination process, the chosen modified bitumens were utilized in the Marshall mix design to determine the OBC. Lastly, mechanical performance tests were detailed to evaluate the performance of asphalt mixtures. The subsequent Chapter will comprehensively delve into the results and engage in discussions closely aligned with the research objectives.

CHAPTER 4

RESULTS AND DISCUSSION

This Chapter presents the outcomes and discussions of laboratory experimental investigations. The primary focus of the study is to meticulously evaluate the effect of modified waste cooking oil granulates on bitumen properties, including rheological, morphological, and chemical aspects. Furthermore, the scope extends to studying the effect of WCO on the mechanical performance of asphalt mixtures, considering various ratios of modified WCO granulates. The modified waste cooking oil granulates (MWCOG) were added to bitumen by 5%, 10%, 15%, 20%, and 25% by weight of base bitumen to produce the modified bitumen for each ratio (45:55 and 50:50). The obtained results of WCO modified bitumen and the asphalt mixtures are discussed in accordance with the work sequence outlined in Chapter 3.

4.1 Materials characterisation (Objective-01)

The materials needed for bitumen modification and mixture development underwent thorough assessment and testing, adhering to stringent criteria. The first section of Objective 01 of the study mainly focuses on and is limited to the basic properties of the 60/70 grade bitumen, granite aggregates, SBS and waste cooking oil. However, the second section delves into the properties of modified waste cooking oil, its modification process with SBS, and the morphological and chemical analysis of modified waste cooking oil granulates (MWCOG). The final section of Objective 01 emphasizes identifying the optimum ratio of MWCOG through the trial and error method.

4.1.1 Properties of Bitumen

Penetration grade 60/70 bitumen was employed in this study owing to its widespread use in the pavement industry of Malaysia. The stringent evaluations were undertaken to assess the suitability of the bitumen, ensuring its adherence to standard specifications for practical use. The physical and the rheological properties parameters of most importance were tested in accordance with the standard testing procedures. The physical evaluation of the bitumen involved conducting penetration tests at 25°C, determining the softening point, assessing rotational viscosity at 135 °C and 165 °C, and measuring the specific gravity. These parameters were examined to validate the selection criteria for the bitumen. Table 4.1 presents the test results, indicating a penetration of 62.1 dmm for the base bitumen and a softening point temperature of 46.5 °C. Notably, the softening point falls within the specified range, though closely approaching the minimum criteria of 48 °C. Likewise, the rotational viscosity is below the specified maximum limit of 3 Pa.s, meeting the established criterion.

Table 4.1: Empirical test results of base bitumen

Property Test	Result	Specification	Standard	Status
Penetration @ 25°C (dmm)	62.1	60-70	(ASTM D5, 2019)	Passed
Softening point (°C)	46.5	48	(ASTM D36, 2008)	Close to max
Specific gravity	1.03	-	(ASTM D70, 2021)	-
Brookfield Viscosity @ 135°C	0.429	3.0 Pa.s	(ASTM D 4402, 2000)	Passed
Ductility @ 25 °C (cm)	101	≥100	(ASTM D 113-07, 2002)	Passed
Mass loss (%)	0.1	1.0 max	(ASTM D2872-22, 2022)	Passed
Flash and Fire Test	255&265	250&-	(ASTM D92, 2007)	Passed
Rutting Parameter (Unaged), kPa @ 64 °C	1.01	1.0 min	(ASTM 7175, 2001)	Passed
Rutting Parameter (aged), kPa 64 °C	2.38	2.2 min	(ASTM 7175, 2001)	Passed
Fatigue Parameter (PAV-aged), kPa 28 °C	3200	5000 max	(ASTM 7175, 2001)	Passed

Furthermore, the base bitumen 60/70 underwent extended characterization to assess rheological parameters under both aged and unaged conditions. The rutting parameter, measured at 64 °C before and after short-term ageing, remained within specification, with values of 1.01 kPa and 2.38 kPa, respectively. Fatigue parameters also met the specified threshold of 5000 kPa at 28 °C. Additionally, the RTFO mass loss was less than 1.0%, meeting the prescribed criterion. In summary, the 60/70 penetration grade bitumen successfully adheres to the standard specifications outlined by JKR. Detailed results, along with associated specifications and standards, are provided in Table 4.1.

4.1.2 Properties of aggregates

In this study, granite aggregates were chosen for asphalt mixture preparation owing to their abundant availability and the proximity of quarries near UPM. Additionally, the preference for granite aggregates is attributed to their low abrasion and high strength, distinguishing them favourably from other available types of aggregates. Table 4.2 displays the laboratory tests and aggregate performance results.

Table 4.2: Granite aggregate test results

Property Test	Values measured	Specification	Standard	Status
Los Angeles Abrasion (%)	20.23	30 max	(ASTM C131/C131M-14, 2014)	Passed
Flakiness and Elongation	11.4 & 1.27	<20	(ASTM 4791, 2019)	Passed
Aggregate impact value	9.88	15 max	(ASTM D5874, 2016)	Passed
Specific gravity coarse	2.56	-	(ASTM C127, 2004)	-
Specific gravity fine	2.62	-	(ASTM C128, 2015)	-
Soundness of aggregates (sodium sulphate) %	0.6	12 max	(ASTM C 88, 1999)	Passed

In the comprehensive assessment of aggregate properties, the Los Angeles Abrasion test revealed a nominal abrasion value of 20.23%, conforming to the stipulated

criterion of 30%. Further scrutiny of flakiness and elongation characteristics yielded values of 11.4% and 1.27%, respectively, both falling below the 20% threshold. Whereas the Aggregate impact value test resulted in 9.88%, indicating compliance with the prescribed maximum limit of 15% outlined. The soundness test showed 0.6%, well below the 12% maximum. These results of the aggregate testing collectively fulfilled the criteria to be used in the preparation of asphalt mixtures as following the JKR specifications.

4.1.3 Properties of waste cooking oil and Styrene butadiene styrene

The collected waste cooking oil (WCO) was obtained from various households and underwent an examination of fundamental properties and visual characteristics. Notably, the WCO exhibited a dark brown colour, attributed predominantly to the frying activities and residual matter. In contrast, typical cooking oil tends to possess lower viscosity. This observation was substantiated by viscosity measurements at 40 °C, revealing a notably low viscosity of 41.7 cp, further confirming the distinct characteristics of the collected waste cooking oil. On the other hand, styrene butadiene styrene (SBS) with a composition ratio of 30/70 (S/B) was employed for the modification of waste cooking oil (WCO), a prevalent choice in the pavement industry. The SBS utilized in the study exhibits a tensile strength of 24 MPa and a hardness value of 74. Additionally, the specific gravity of the SBS is measured at 0.94 g/cm³, highlighting its lightweight nature. The comprehensive properties of both the WCO and SBS are precisely detailed in Table 4.3.

Table 4.3: Waste cooking oil and SBS properties results

Material	Properties	Result
WCO	Appearance	Viscous Liquid
	Viscosity @ 40 °C (cp)	41.7
	Colour	Dark brown
	Flash Point (°C)	278
SBS	S/B block ratio (%)	30/70
	Tensile strength (MPa)	24
	Hardness	74
	Elongation at break (%)	800
	Melt index/g/10min	<1
	Specific gravity(g/cm ²)	0.94

4.2 Properties of modified waste cooking oil granulates

In this study, the raw waste cooking oil (WCO) transformed into a rubbery solid state as a necessary step before its incorporation into bitumen for modification. This modification was undertaken to ensure a strong compatibility between the modifier and bitumen. The pre-processing and modification of the raw WCO were imperative to address shortcomings identified in prior research efforts. The resulting material, a blend of raw WCO and varying proportions of SBS formed into small bead shapes, is referred to as Modified Waste Cooking Oil Granulates (MWCOG). The detailed pre-processing and the modification process are discussed in section 3.3.3. The subsequent sections discuss in detail the physical, morphological and chemical properties of MWCOG.

4.2.1 Physical properties modified WCO granulates

The processed and modified Waste Cooking Oil granulates have undergone a transformation into a solid, rubbery state, showcasing distinct physical properties compared to the original characteristics of raw WCO discussed earlier in Section 4.1.3.

A detailed summary of these altered properties is presented in Table 4.4. Notably, the appearance of the WCO post-modification with SBS has evolved into a semi-solid or rubbery structure, exhibiting a yellowish-brown colour in contrast to the dark brown hue observed before the filtration process. This change underscores the impact of the modification process on the visual and structural attributes of the WCO. The MWCOG have been sliced into small granulates, each measuring ≤ 2 cm, facilitating a more uniform blending with the bitumen, as illustrated in Figure 3.4. The reduced size of these granulates offers an increased surface area, thereby minimizing the dissolution time into the bitumen. This deliberate size reduction enhances the efficiency of the blending process, ensuring improved integration of the modified WCO with the bitumen matrix. The blending process of polymers with bitumen typically demands elevated temperatures exceeding 150 °C to ensure complete melting and integration within the bitumen matrix. In contrast, the MWCOG exhibit a notably lower melting temperature of 132 °C. This lower temperature requirement indicates a swift blending process, characterized by efficiency with minimal time and temperature constraints.

Table 4.4: Basic properties of modified WCO granulates

Material	Property	Result
Modified WCO (45:55 and 50:50)	Appearance	Semi-solid
	Colour	Yellowish brown
	size (cm)	≤ 2
	Density	0.9
	Melting point (°C)	132

4.2.2 Surface morphology of MWCOG

The microscale morphologies of modified waste cooking oil granulates and modified bitumen were examined by using FESEM. Figure 4.1 depicts the morphology and

surface texture of the MWCOG-45-55 and MWCOG-50:50 at magnifications of 1 mm and 100 μm . It can be interpreted that the modification of the waste cooking oil with SBS has produced a rubbery solid material with clear physical homogeneity and non-presence of the SBS. The homogeneity of SBS and WCO is mainly caused due to the swelling of the SBS particles by absorbance of the WCO (Niu et al., 2021b; Saboo et al., 2021a).

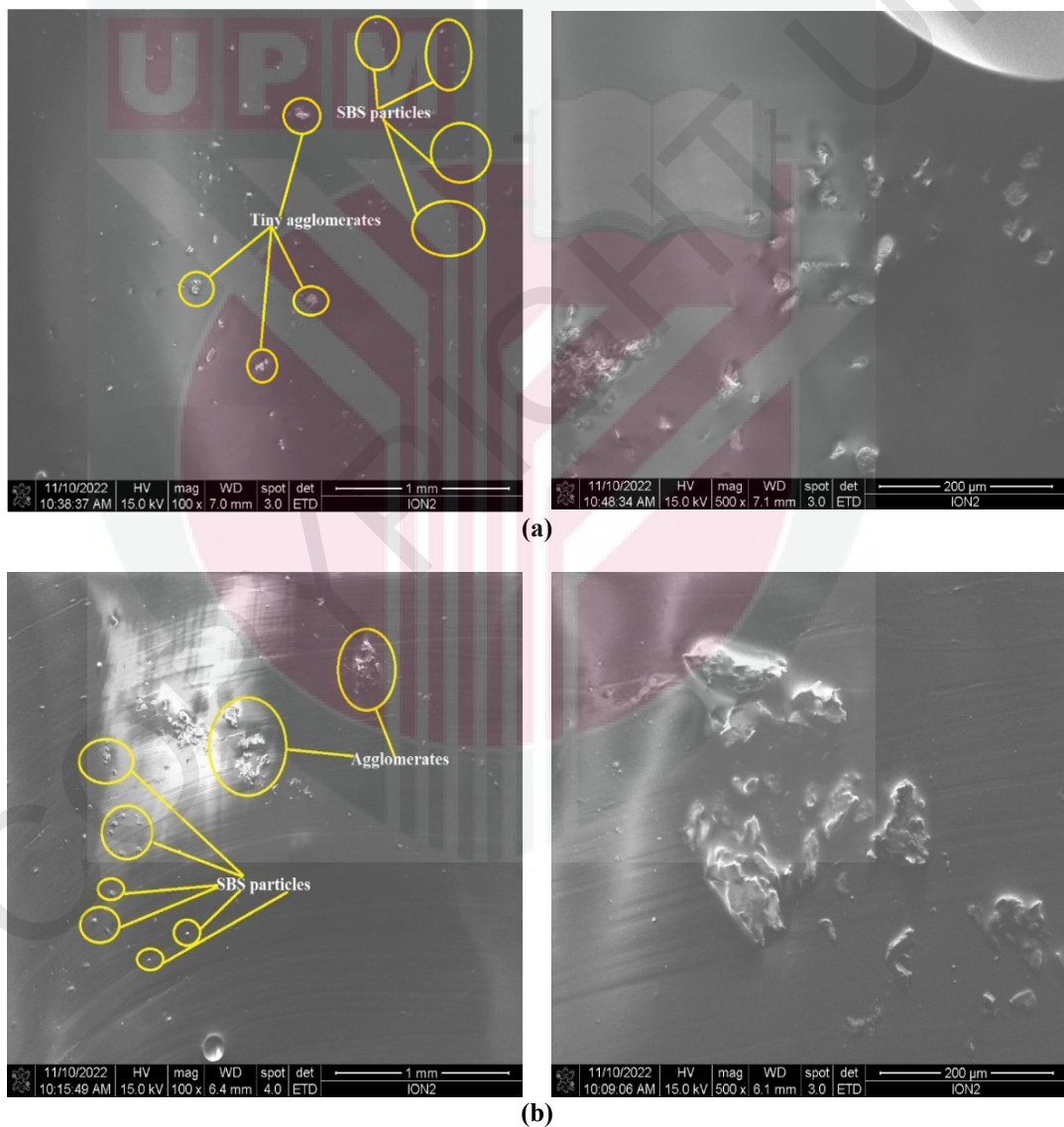


Figure 4.1: FESEM images of modified waste cooking oil: (a) 45:55 (b) 50:50

Conversely, the FESEM micro images of MWCOG-45-55 and MWCOG-50:50 have illustrated the appearance of the SBS particles with different sizes and shape structures. Figure 4.1 depicts the images of the MWCOG-45-55 and MWCOG-50:50 and it can be noticed that the appearance of the SBS particles on MWCOG-45-55 is comparatively less than the MWCOG-50:50. As expected, the higher content of the WCO in the modification process has significantly dissolved the SBS particles with minimum peculiarities. However, Figure 4.1a has demonstrated the few agglomerates which may be caused due to the excessive WCO absorbance by SBS particles. In contrast, the MWCOG-50:50 has more non-homogeneity and appearance of the SBS particles due to the equivalent ratio of the WCO and SBS. Furthermore, the size and structure of the SBS have significantly changed after the modification process with WCO as shown in the FESEM images (Figure 4.1). The average particle sizes of SBS used during the process of modification compared with the size in the SEM images conclude the significant reduction in the size of SBS. Similarly, the fractured surface of the SBS within the MWCOG inferred that it creates better adhesion with the bitumen.

4.2.3 Energy-dispersive X-ray (EDX) of MWOGs

The energy-dispersive X-ray (EDX) analysis was conducted in conjunction with the mapping technique to further clarify the elemental composition of the MWCOG. The EDX analysis is useful for the identification of the elemental composition while the mapping further enhances the conception of the microscale distribution. Figure 4.2 and Figure 4.3 presents the EDX of the MWCOG-45-55 and MWCOG-50:50 respectively. The EDX analysis of the MWCOG discerns a notable concentration of carbon. The

observed increased carbon content in the composite structure of SBS and WCO is attributed to their inherent hydrocarbon structures. This inherent composition significantly contributes to the higher carbon content, aligning with the polymer characteristics of SBS (Zhu et al., 2014). Additionally, the organic nature of WCO imparts a noteworthy increase in the overall carbon content within the MWCOG. These findings provide valuable insights into the elemental composition of MWCOG, important for understanding their structural properties. Furthermore, the results highlight the spatial distribution of carbon within the composite, aligning with the polymeric structure of SBS and the organic composition of WCO (Table 4.5). This emphasizes the successful amalgamation of both constituents in the composite material.

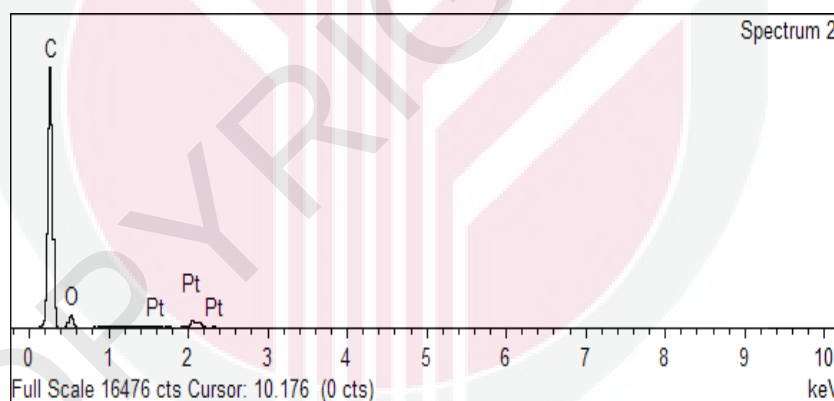


Figure 4.2: EDX spectra of modified WCO ratio 45:55

Table 4.5: Elemental composition of MWCOG-45:55

Element	Weight (%)	Atomic (%)	Energy level
Carbon (C)	82.24	88.92	K shell
Oxygen (O)	13.28	10.78	K shell
Platinum (Pt)	4.48	0.30	M shell
Total	100		

The observed carbon higher concentration in the composite material (MWCOG) holds a noteworthy implication for the materials in terms of durability, thermal stability and mechanical strength (Saboo et al., 2021b). Conversely, the oxygen lower content in composite material may be attributed to the inherent composition of the SBS and WCO (Rodrigues et al., 2020). The carbon abundance nature of the SBS and the dominance of the triglycerides which are rich in carbon in WCO contribute slightly to the oxygen signal (Azahar et al., 2016d). The minor variation in the carbon and oxygen content in the MWCOG-45-55 and MWCOG-50:50 can be attributed to the minimal variation in the ratio of SBS and WCO. The presence of platinum in the results is not indicative of the material's inherent chemical composition. Instead, it arises from the coating applied to enhance conductivity for more effective analysis purposes.

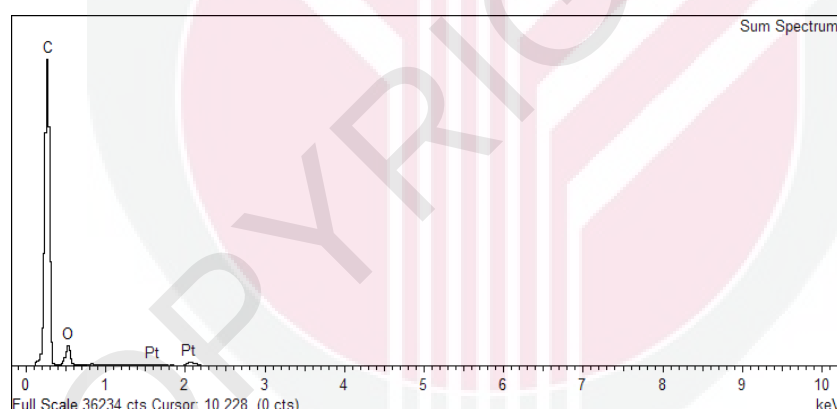


Figure 4.3: EDX spectra of modified WCO ratio 50:50

Table 4.6: Elemental composition of MWCOG-50:50

Element	Weight (%)	Atomic (%)	Energy level
Carbon (C)	81.75	86.85	K shell
Oxygen (O)	16.33	13.03	K shell
Platinum (Pt)	1.92	0.13	M shell
Total	100		

4.3 Identification of optimal MWCOG ratio

In this study the filtered WCO was modified by blending the SBS: WCO at various of 20:80, 30:70, 40:60, 45:55 and 50:50. However, it is necessary to opt for the promising performing MWCOG. The performance of bitumen modified with MWCOG tends to decrease with higher WCO content, while a higher content of SBS primarily results in significantly improved properties. The optimum ratio is desirable for bitumen modification which could provide some balanced properties. Therefore, the study involved blending the modified waste cooking oil granulates (MWCOG) with base bitumen at various ratios, specifically 20:80, 30:70, 40:60, 45:55, and 50:50, with concentrations of 5%, 10%, 15%, 20%, and 25% by weight. These blended modified bitumens underwent testing for rotational viscosity and rutting parameters at different temperatures. Each tested bitumen underwent a comprehensive analysis to assess its suitability for further evaluation. The study determined the mixing and compaction temperatures and identified the performance grade of the modified bitumen to identify the best-performing blends. In the subsequent section, the MWCOG-20:80 and MWCOG-50:50 will be discussed in detail to evaluate the comparison between the higher and the lower content of WCO within the bitumen matrix. All other MWCOG modified bitumen results are presented in **Appendix A** while this section summarises the promising ratios of MWCOG.

4.3.1 Modified WCO granulates-20:80 and 50:50

The results of the rotational viscosity conducted within a temperature range from 90 °C to 165 °C and with the incorporation of the MWCOG-20:80 and MWCOG-50:50

by weight percentage of bitumen varying from 5% to 25% are presented in Table 4.7 and Table 4.8 while illustrated in Figure 4.4 and Figure 4.5. It can be observed that the base bitumen viscosity at temperatures of 90 °C and 165 °C is 5770.2 cp and 138.8 cp respectively. It has been observed that the addition of the MWCOG-20:80 significantly decreased the viscosity of the modified bitumens. As expected, the MWCOG-50:50 have enhanced the modified bitumens viscosities. The results revealed that the viscosity of the 20:80-5% at 90 °C is 5467.8 cp which is 5.2% lower than the base bitumen as shown in Figure 4.4.

Table 4.7: Rotational viscosity results of modified bitumen at 20:80

Blend type	Viscosity (cp)				Slope (cp/°C)	
	90 °C	110 °C	135 °C	165 °C	Zone-I	Zone-II
Base	5770.2	1557.6	429	138.8	210.6	37.6
20:80-5%	5467.8	1297.5	339.7	107.9	208.5	31.9
20:80-10%	4199.9	1054.6	287.4	102.0	157.3	25.6
20:80-15%	3941.8	979.2	299.9	100.0	148.1	22.6
20:80-20%	3099.9	1000.1	309.9	110.0	105.0	23.0
20:80-25%	2814.9	711.5	312.0	124.9	105.2	13.3

Consequently, the further addition of the MWCOG-20:80 into the base bitumen demonstrates a similar decrement in the viscosity while the performance of the MWCOG-50:50 is otherwise (Figure 4.5). The results indicate that the viscosity of 20:80-5% at 135 °C is 339.7 cp which is lower than the 50:50-5% viscosity of 562 cp. The 50:50-5% demonstrates a 65 % higher viscosity than the 20:80-5%. The outcomes suggest that the lower quantity of the WCO within the bitumen matrix provides better performance of modified bitumen in terms of viscosity compared to the higher WCO (Wang et al., 2018). The addition of the MWCOG-20:80 has caused the softening of the bitumen due to the higher content of the oil within the composite material.

Table 4.8: Rotational viscosity results of modified bitumen at 50:50

Blend type	Viscosity (cp)				Slope (cp/°C)	
	90 °C	110 °C	135 °C	165 °C	Zone-I	Zone-II
Base	5770.2	1557.6	429	138.8	210.6	37.6
50:50-5%	7744.1	2276.9	562.0	183.3	273.4	57.2
50:50-10%	7950.0	3469.1	946.0	307.6	224.0	84.1
50:50-15%	8500.0	4300.0	1682.7	494.3	210.0	87.2
50:50-20%	8900.0	5700.0	2127.3	809.5	160.0	119.1
50:50-25%	9700.0	6100.0	2988.2	1360.2	180.0	103.7

Figure 4.4 and Figure 4.5 demonstrates the two different slopes variation i.e., the slope of zone-I and zone-II. The slope of zone-I ranges between 90 °C to 110 °C whereas zone-II is between 110 °C and 165 °C. The curves of the modified bitumen reveal that zone-I has a higher slope which corresponds to the higher viscosity of the bitumen whereas zone-II has a lower slope with lower viscosity. The significant reduction in the slope is caused by the increase in the testing temperature and due to the higher content of the waste cooking oil within the bitumen matrix. However, the MWCOG-20:80 has a steep slope at zone-I while the MWCOG-50:50 demonstrate a minor slope variation. Similarly, the zone-II of MWCOG-50:50 has a major difference of 66.1% which is higher than the 24.3 % of MWCOG-20:80. It is noteworthy that the MWCOG-50:50 has demonstrated better performance at higher temperatures with higher slope variation. The variation in the slope (%) of zone-I and zone-II is presented in Table 4.7 and illustrated in Figure 4.4 and Figure 4.6. It can be seen that the increasing content of MWCOG-20:80 causes the reduction of the slope for zone-I and zone-II.

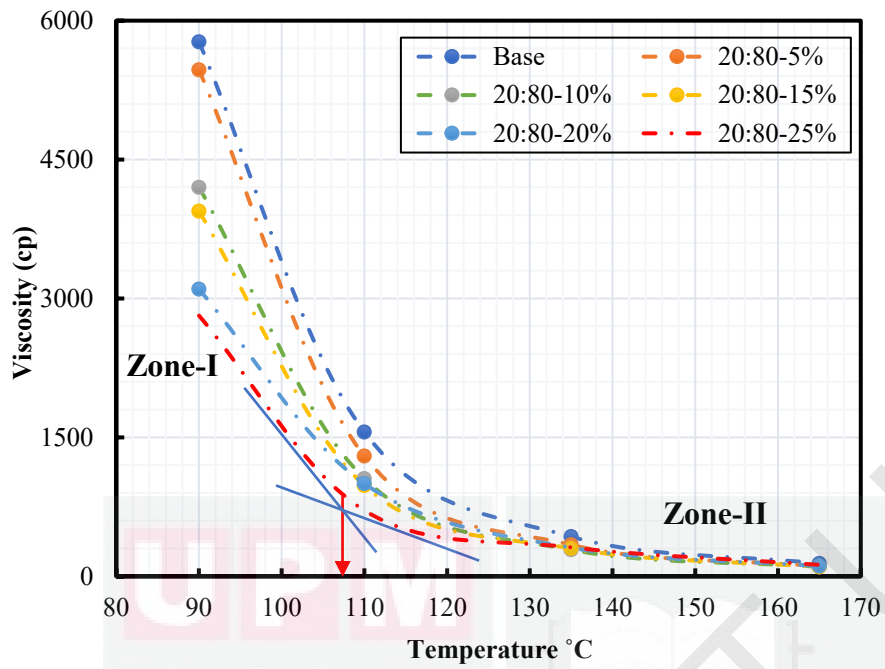


Figure 4.4: Viscosity results of 20:80 modified bitumen at varying temperatures

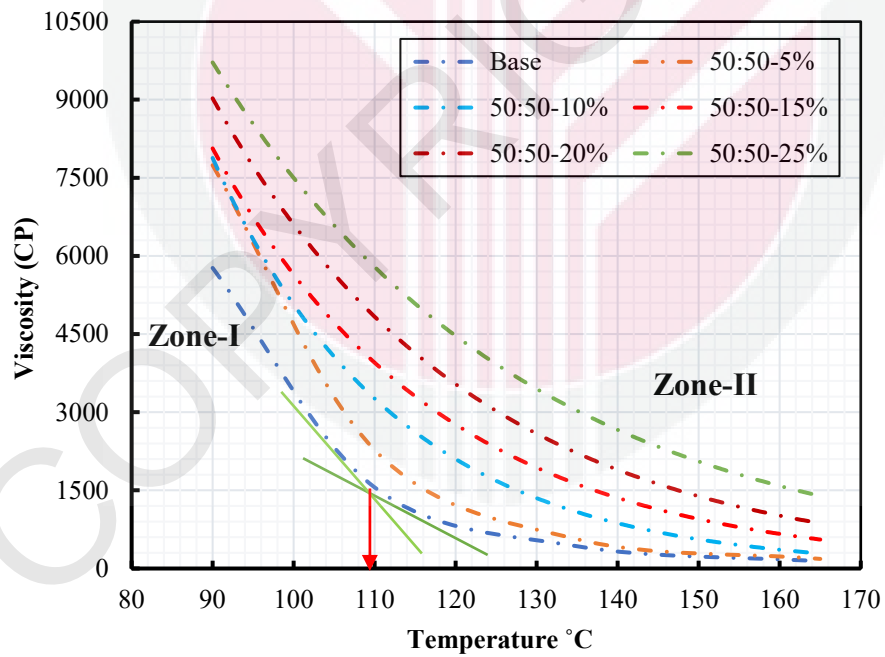


Figure 4.5: Viscosity results of 50:50 modified bitumen at varying temperatures

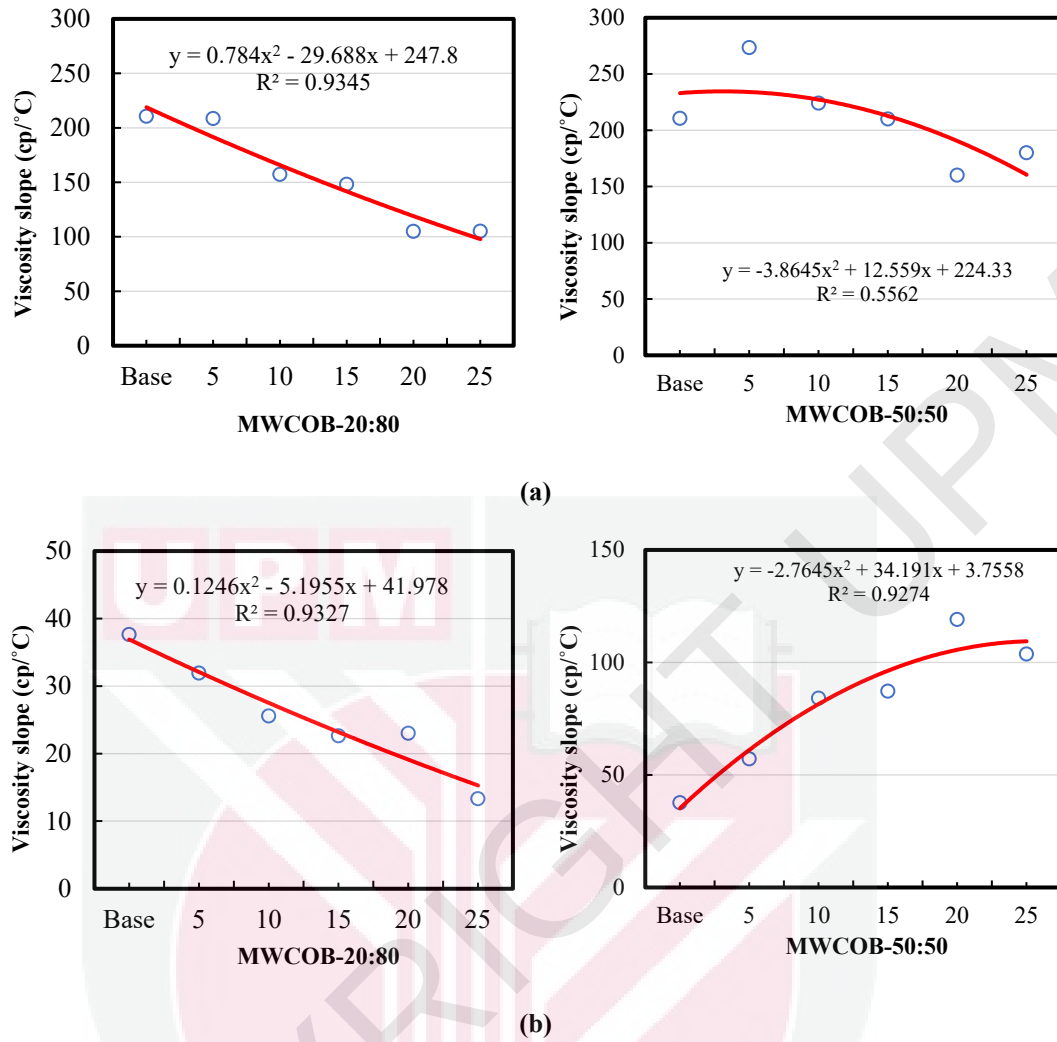


Figure 4.6: Viscosity slope of 20:80 and 50:50 modified bitumen at (a) zone-I (b) zone-II

However, the total reduction percentage of zone-I is significantly higher than that of zone-II which may be due to the stiffness of the bitumen at lower temperatures.

Whereas zone-II demonstrates minor variations in modified bitumen variations as the viscosity of bitumen has already dropped notably compared to that of zone-I. On the other hand, MWC0G-50:50 has shown improvement in zone-II with minor slope variation as expected due to the higher viscosity on incorporating the MWC0G. The overall pattern of reduction in the viscosity and the slope elucidates the decrease in the performance of the modified bitumen in comparison to the base bitumen on incorporating the MWC0G-20:80. Whereas MWC0G-50:50 has shown the increase

in the zone-II of the viscosity curves which is desirable. The viscosity slope of MWCOD-20:80 and MWCOD-50:50 mixtures generally follows a strong relationship with temperature, as indicated by high R^2 values (0.9345 and 0.9327, respectively). These results suggest that the data fits the model well, reflecting consistent behavior of viscosity changes with temperature. However, zone-I of MWCOD-50:50, showed a weaker correlation with a lower R^2 of 0.5562, indicating more variability in its viscosity response. This difference suggests that the composition ratio influences the predictability of viscosity behavior.

Furthermore, the temperature and the viscosity relationship are important to evaluate the bitumen mixing and the compaction temperatures. The viscosity of the bitumen is mainly associated with pumping and mixing at the hot mix plant. The higher the viscosity of the bitumen the higher will be the mixing and the compaction temperature and vice versa. Whereas lower viscosity leads to the rutting of the pavements. Therefore, the optimum viscosity with managed temperature is desirable for sustainable pavements. The mixing and the compaction temperatures of the MWCOD-20:80 and MWCOD-50:50 are provided in Table 4.9 and Table 4.10 while Figure 4.7 depicts the temperatures at corresponding viscosities of 0.28 ± 0.02 and 0.17 ± 0.03 respectively.

Table 4.9: Mixing and compaction temperatures of 20:80 modified blends

Blend type	Viscosity (Pa.s)		Mixing temperature °C	Compaction temperature °C
	135 °C	165 °C		
Base	0.429	0.138	160	145
20:80-5%	0.395	0.108	155	144
20:80-10%	0.287	0.102	149	144
20:80-15%	0.300	0.110	150	144
20:80-20%	0.310	0.125	154	135
20:80-25%	0.312	0.136	157	135

Table 4.10: Mixing and compaction temperatures of 50:50 modified blends

Blend type	Viscosity (Pa.s)		Mixing temperature °C	Compaction temperature °C
	135 °C	165 °C		
Base	0.429	0.138	160	145
50:50-5%	0.562	0.183	166	154
50:50-10%	0.946	0.308	180	164
50:50-15%	1.683	0.494	192	168
50:50-20%	2.127	0.810	>200	180
50:50-25%	2.988	1.360	>200	>200

A similar trend has been observed in the viscosity-temperature relationship plot. The increasing content of the MWCOG-20:80 has demonstrated a decrement in the mixing and the compaction temperature. Generally, the decreased trend in temperature is desirable for sustainable construction of the pavements. Nevertheless, the variations in the viscosities at temperatures 135 °C and 165 °C are minor which leads to insufficient temperature variations. On the other hand, MWCOG-50:50 have shown higher mixing and compaction temperatures in comparison to the MWCOG-20:80. The findings suggest that the higher viscosities lead to higher temperatures. The mixing temperature of the base bitumen is 160 °C and for the 20:80-5% is 155 °C with only a difference of 5 °C. The addition of the MWCOG-50:50 into bitumen causes the stiffening of modified bitumens as the waste cooking oil content in composite material is low. The 50:50-5% demonstrated a mixing temperature with a minimum variation of 6 °C compared to base bitumen. This reveals that the MWCOG-50:50 are performing better with increased viscosity.

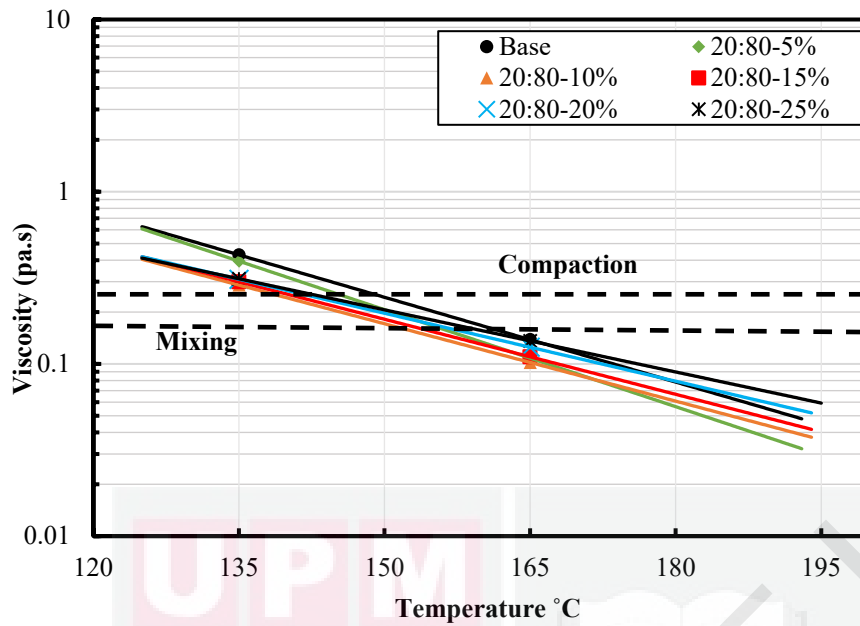


Figure 4.7: Viscosity-temperature relationship of 20:80 blends

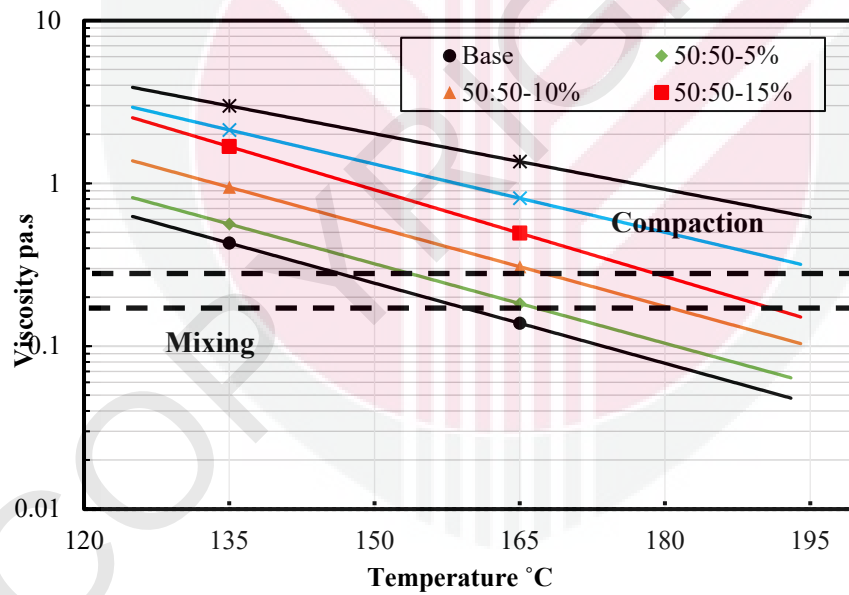


Figure 4.8: Viscosity-temperature relationship of 50:50 blends

The overlap of the curves of the modified bitumen with MWCOG-20:80 reflects the negative influence of the high quantity of waste cooking oil on the bitumen properties.

Table 4.11 provides the viscosity shift factors at temperatures of 135 $^{\circ}\text{C}$ and 165 $^{\circ}\text{C}$.

It can be observed that the variation between the shift factors of various modified bitumen with MWCOG-20:80 is minor which further validates the obtained results of temperature-viscosity relationship. However, the shift factors of MWCOG-50:50 modified bitumen are high and each percentage incorporated demonstrated a higher variation in shift factors. Moreover, the zone-II has shown a significant improvement in the shift factors which reflects the enhancement of the viscosity at higher temperatures. Thus, the MWCOG-50:50 show a promising performance in comparison to the base and the MWCOG-20:80 modified bitumens.

Table 4.11: Shift factors and slope (%) of 20:80 modified bitumen

Blend type	Shift factor		Slope (%)	
	135 °C	165 °C	135 °C	165 °C
Base	-	-	-	-
20:80-5%	-21.09	-21.91	-1.81	-0.61
20:80-10%	-33.19	-26.25	-1.43	-0.36
20:80-15%	-30.17	-20.46	-0.86	-0.19
20:80-20%	-27.84	-9.62	-0.60	-0.07
20:80-25%	-27.37	-1.66	-0.47	-0.01

Table 4.12: Shift factors and slope (%) of 50:50 modified bitumen

Blend type	Shift factor		Slope (%)	
	135 °C	165 °C	135 °C	165 °C
Base	-	-	-	-
50:50-5%	30.84	32.10	2.65	0.89
50:50-10%	120.23	122.42	5.17	1.69
50:50-15%	291.69	257.48	8.35	2.37
50:50-20%	395.11	485.68	8.49	3.36
50:50-25%	595.58	883.51	10.23	4.89

The MWCOG-20:80 modified bitumens are further characterized by determining the rheological properties at varying temperatures ranging from 52 °C to 82 °C using the dynamic shear rheometer (DSR). The bitumen generally demonstrates viscoelastic properties and depends on the variation of the temperature and the loading frequency. The rutting parameters of MWCOG-20:80 and MWCOG-50:50 are provided in Table

4.13 and Table 4.14 and depicted in Figure 4.9 and Figure 4.10 respectively. The rutting parameter ($G^*/\sin\delta$) of the MWCOG modified bitumen was determined at 1.59 Hz in accordance with SHRP. The resistance against the rutting is mainly assessed by the $G^*/\sin\delta$ for the bitumen and the modified bitumens. It can be observed from the results that the incorporation of the MWCOG-20:80 into the bitumen causes a reduction in the rutting resistance of the modified bitumen whereas the performance of the MWCOG-50:50 is otherwise. The performance of the modified bitumen is consistent with earlier discussed results of the rotational viscosity. The $G^*/\sin\delta$ of base bitumen at 64 °C is 1.43 kPa while the 20:80-15% and 50:50-15% are 1.06 kPa and 5.22 kPa respectively.

Table 4.13: Rutting parameter of 20:80 at varying temperatures

Blend type	Rutting parameter (kPa)					
	52°C	58°C	64°C	70°C	76°C	82°C
Base	7.07	3.16	1.43	0.65	0.33	0.23
20:80-5%	4.96	2.41	1.11	0.55	0.30	0.21
20:80-10%	4.56	2.90	1.41	0.81	0.47	0.32
20:80-15%	3.38	1.90	1.06	0.64	0.34	0.22
20:80-20%	3.12	2.45	1.69	1.26	0.68	0.31
20:80-25%	3.92	3.00	2.47	1.84	0.92	0.42

Table 4.14: Rutting parameter of 50:50 at varying temperatures

Blend type	Rutting parameter (kPa)					
	52°C	58°C	64°C	70°C	76°C	82°C
Base	7.07	3.16	1.43	0.65	0.33	0.23
50:50-5%	9.6	3.5	1.7	0.8	0.4	0.3
50:50-10%	12.62	6.11	3.70	1.74	1.09	0.71
50:50-15%	16.40	8.48	5.22	2.43	1.50	0.79
50:50-20%	19.09	9.78	5.78	3.11	1.96	1.05
50:50-25%	46.35	14.85	7.15	4.31	2.91	2.21

However, it can be observed that on higher content of the MWCOG i.e., 20:80-20% and 20:80-25% the rutting parameter is higher than base bitumen with values of 1.69 kPa and 2.47 kPa respectively. On the other hand, the increasing temperature beyond 64

°C demonstrates the likewise performance of the modified bitumen with minimum variation compared to the base bitumen. The outcomes suggest that all the modified bitumen is failing between 64 °C to 70 °C which corresponds to the PG64 regardless of the 20:80-20% and 20:80-25% which are failing beyond the 70 °C as PG70. Furthermore, the performance of the modified bitumen with MWCOG-50:50 is higher than the base and the MWCOG-20:80. As expected, the content of WCO within the composite material is lower while the SBS is higher which ultimately leads to enhanced performance. It can be seen that the 50:50-20% and 50:50-25% demonstrated a failing temperature of 76 °C and 82 °C which corresponds to the PG76 and PG8 respectively. Therefore, it can elucidate that the MWCOG-50:50 is showing a promising performance with improved bitumen grading.

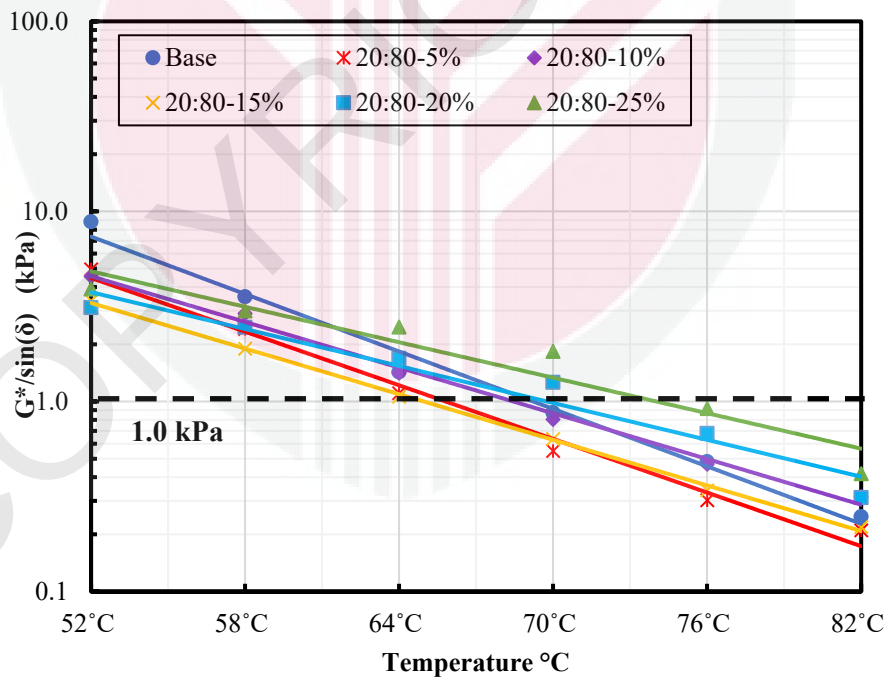


Figure 4.9: Temperature effect on rutting parameter of 20:80 modified blends

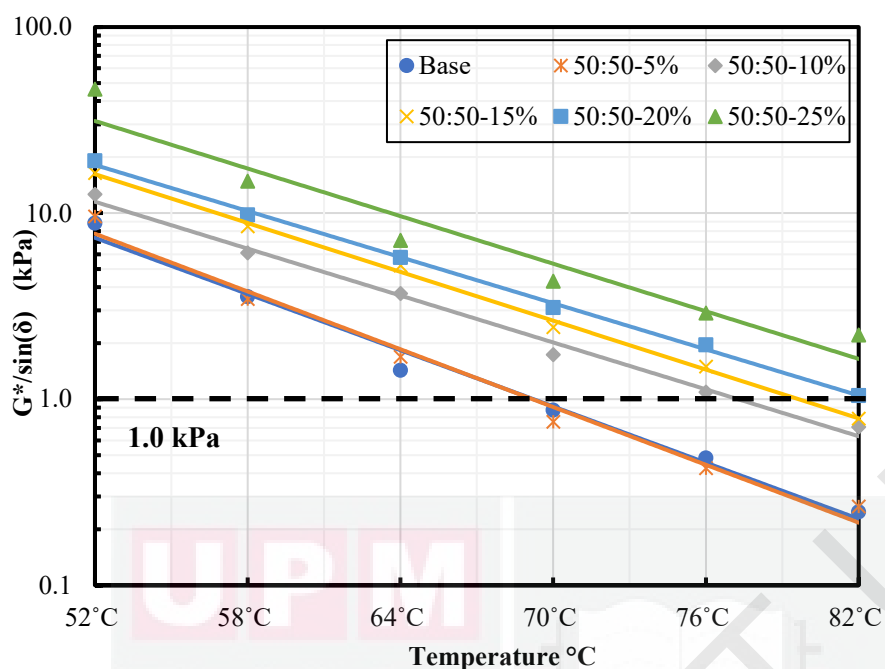


Figure 4.10: Temperature effect on rutting parameter of 50:50 modified blends

4.4 Summary of identification of optimal ratio of MWCO granulates

Table 4.15 presents the overall summarized findings of the MWCOG modified bitumens at various ratios (20:80, 30:70, 40:60, 45:55 and 50:50). The results discussed in a previous section of MWCOG-20:80 and MWCOG-50:50 have demonstrated the varied properties. The MWCOG-20:80 in which the WCO content is very high has shown a lower performance compared to the base bitumen. Whereas the MWCOG-50:50 performed extremely better which enhanced properties. It can be observed from the summarized results in Table 4.15 that the viscosity of the modified bitumen at 135 °C is linearly increasing as the WCO content is decreasing. The 20:80-5%, 30:70-5%, 40:60-5%, 45:55-5% and 50:50-5% have viscosities of 0.395, 0.428, 0.493, 0.513 and 0.562 Pa. s respectively. A 42% improvement has been observed in rotational viscosity of 50:50-5% at 135 °C compared to 20:80-5% while the 45:55-5% demonstrates a 29% improvement. Similarly, the failing temperatures of all

modified bitumen have improved and achieved better performance grading. For instance, the 20:80-15%, 30:70-15%, 40:60-15%, 45:55-15% and 50:50-15% have achieved the performance grading of PG64, PG70, PG76, PG76, and PG82. Furthermore, the rutting parameter at 64 °C for 50:50-15% and 45:55-15% is 5.22 kPa and 2.44 kPa which is 79.6 % and 56.6 % higher than the 20:80-15% respectively. In summary, the overall performance of the MWCOG-45:55 and MWCOG-50:50 is promising in terms of rotational viscosity and dynamic rheological properties. Therefore, these two ratios have been selected for further evaluation to assess their impact on various parameters related to bitumen properties and mechanical performance.

Table 4.15: Summarised results of modified bitumen blends at various modified WCO ratios

Blend type	Viscosity (Pa.s)		Compaction temperature °C	Mixing temperature °C	Rutting @ 64 °C (kPa)	Failure temperature °C	Performance grading
	135 °C	165 °C					
Base	0.429	0.138	145	160	1.43	67.8	64
20:80-5%	0.395	0.108	144	155	1.11	64.1	64
20:80-10%	0.287	0.102	144	149	1.41	67.7	64
20:80-15%	0.300	0.110	144	150	1.06	64.2	64
20:80-20%	0.310	0.125	135	154	1.69	72.8	70
20:80-25%	0.312	0.136	135	157	2.47	75.7	70
30:70-5%	0.428	0.119	143	156	1.38	66.7	64
30:70-10%	0.396	0.140	147	160	1.74	68.1	64
30:70-15%	0.405	0.170	153	165	1.83	72.9	70
30:70-20%	0.544	0.220	158	170	2.14	76.0	76
30:70-25%	0.685	0.210	158	172	3.53	81.3	76
40:60-5%	0.493	0.164	150	165	1.29	66.9	64
40:60-10%	0.662	0.213	159	171	2.25	71.1	70
40:60-15%	0.924	0.285	165	179	2.43	76.0	76
40:60-20%	1.160	0.445	181	195	3.19	76.1	76
40:60-25%	1.508	0.545	185	>200	4.98	81.1	76
45:55-5%	0.513	0.150	150	163	1.61	68.2	64
45:55-10%	0.806	0.238	163	173	2.35	72.9	70
45:55-15%	1.350	0.406	174	181	2.44	76.0	76
45:55-20%	1.987	0.550	182	191	3.21	77.1	76
45:55-25%	3.512	1.292	195	>200	5.43	80.1	76
50:50-5%	0.562	0.183	154	166	1.7	67.3	64
50:50-10%	0.946	0.308	164	180	3.70	76.3	76
50:50-15%	1.683	0.494	168	192	5.22	79.9	76
50:50-20%	2.127	0.810	180	>200	5.78	82.0	82
50:50-25%	2.988	1.360	>200	>200	7.15	82.0	82

4.5 Modified WCO bitumen properties at the optimal ratio of MWCOG (Objective 2)

This section of the study comprehensively investigates the MWCOG (45:55 and 50:50) on the characteristics of the bitumen. The modified bitumen was prepared by blending MWCOG by 5%, 10%, 15%, 20%, and 25% by weight of base bitumen. The rotational viscosity and dynamic rheological properties were determined before and after subjecting the bitumen to ageing at various temperature ranges. Furthermore, bitumen homogeneity is assessed through a bitumen separation test, while morphological and chemical analyses have been chosen to further validate the outcomes of modified bitumen.

4.5.1 Rotational viscosity of MWCOG modified bitumen

The viscosity is the bitumen's flow characteristic to assure that it can work easily at a hot mix facility during mixing and pumping. Bitumen with lower viscosity tends to result in pavement rutting, while stiffer bitumen can lead to cracking at lower temperatures. Hence, achieving an optimal grade of bitumen viscosity is essential to meet the requirements of varying climatic conditions. The rotational viscosity of MWCOG-45-55 and MWCOG-50-50 modified bitumen at various content of MWCOG and varying temperatures of 90 °C–165 °C are presented in Table 4.16 and Table 4.17 and illustrated in Figure 4.11 respectively.

Table 4.16: Rotational viscosity of unaged and aged 45:55 modified bitumens

Blend type	Viscosity (cp)							
	90 °C		110 °C		135 °C		165 °C	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Base	5770.2	6572.2	1557.6	2341.7	429	562.9	138.8	153.8
45:55-5%	8211.8	8150.8	2197.3	2954.3	513.3	656.2	150.0	182.3
45:55-10%	7500.0	8700.0	3140.8	3803.4	806.3	1112.2	237.3	237.6
45:55-15%	7800.0	9760.5	2735.0	2686.3	1350.0	1711.9	406.0	459.7
45:55-20%	13300.0	15670.4	5700.0	6720	1987.5	2300.7	550.2	662.0
45:55-25%	15700.0	17654.0	8400.0	9780.1	3512.2	3700.0	1292.3	1006.9

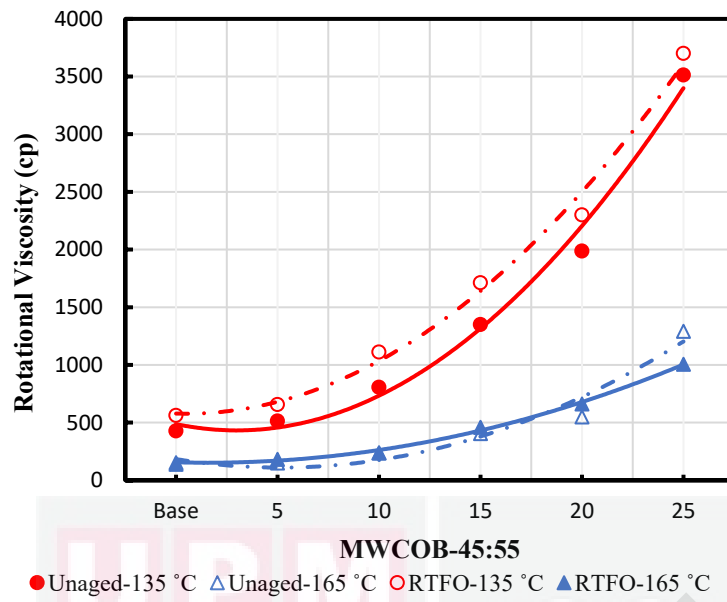
Table 4.17: Rotational viscosity of unaged and aged 50:50 modified bitumens

Blend type	Viscosity (cp)							
	90 °C		110 °C		135 °C		165 °C	
	Unaged	Aged	Unaged	Aged	Unaged	Aged	Unaged	Aged
Base	5770.2	6572.2	1557.6	2341.7	429	562.93	138.8	153.80
50:50-5%	7744.1	9200.0	2276.9	3329.2	562.0	681.4	183.3	193.75
50:50-10%	7950.0	10200.3	3469.1	3049.9	946.0	1349.6	307.6	362.23
50:50-15%	8500.0	11465.0	4300.0	2686.3	1682.7	1962.0	494.3	550.0
50:50-20%	8900.0	13540.0	5700.0	7100.1	2127.3	3864.6	809.5	974.59
50:50-25%	9700.0	15764.0	6100.0	8430.0	2988.2	5587.5	1360.2	1337.0

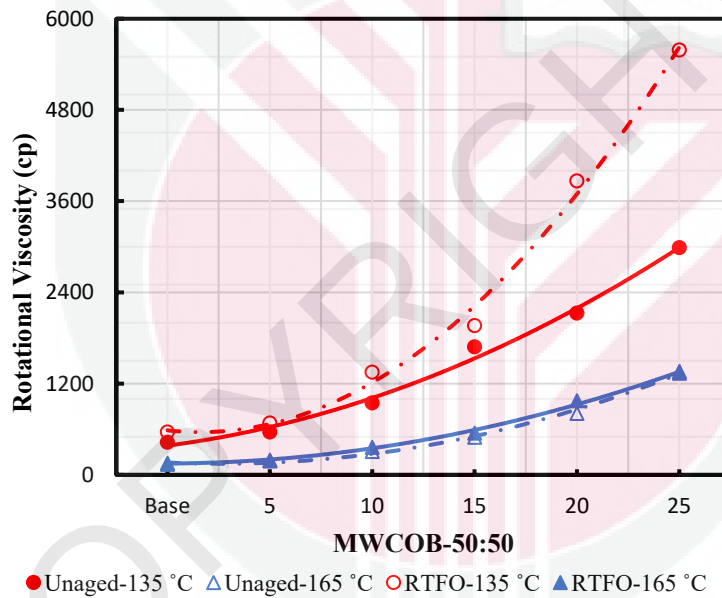
It can be observed that as the test temperature increases, the viscosity of base bitumen and modified bitumen decreases accordingly. Adding 5–25 wt.% of MWCOG-45:55 improves the viscosities in the range of 513–3512.2 cp at 135 °C. However, the MWCOG-50:50 displayed a slightly higher viscosity in the same range with values of 562.1–2988.2 cp than the MWCOG-45:55 (Figure 4.11). The higher viscosities of MWCOG-50:50 are mainly owing to the reduction in the waste cooking oil content and the increment in the SBS content with a ratio of 50:50. The results elucidate that with increasing content of MWCOG, the temperature susceptibility of modified bitumen has enhanced. WCO has a structure similar to that of light components in bitumen. Furthermore, the swelling and the initial cross-linking of the SBS before the modification process within the bitumen matrix promote the adhesion between the bitumen and SBS (Luo et al., 2022a; Zhang et al., 2019). Therefore, the addition of

MWCOG to the base bitumen may have a significant impact on viscosity enhancement in the modification process.

However, Figure 4.11 shows that the viscosity of the 45:55-25% at temperature 135 °C is 3512.2 cp which does not satisfy the SHRP specifications of 3000cp. Therefore, it is evident that the higher content of the MWCOG substantially increases the viscosity confirming the compatibility of the new novel modifier with the bitumen. This demonstrates that the optimal amount of MWCOG needs to be maintained in the blend to get the effectively modified bitumen for the construction of pavements. Similarly, the modified bitumen viscosity has decreased by further increasing the testing temperature to 165 °C. It can be observed that the 45:55-25% and 50:50-25% demonstrated a viscosity of 1292.3 cp and 1360.2 cp at a temperature of 165 °C respectively. Moreover, a likewise trend of viscosity improvement has been observed after the short-term ageing of the modified bitumens. The incorporation of the 25% MWCOG of ratio 45:55 and 50:50 demonstrated a significant enhancement of the viscosities at temperatures 135 °C. The 45:55-25% and 50:50-25% have shown the viscosities of 3700 cp and 5587.5 cp respectively. On the contrary, excessive stiffness of the modified bitumen post-aging is undesirable. Therefore, the incorporation of MWCOG up to 15% is deemed optimal in both cases.



(a)



(b)

Figure 4.11: Rotational viscosity of unaged and aged modified bitumens: (a) 45:55 (b) 50:50

Furthermore, the rate of viscosity increase of the modified bitumen with respect to the base bitumen is provided in Table 4.18 and Table 4.19. It can be elucidated from the outcomes that the MWCOCB incorporation of increasing content significantly improves the viscosity. For instance, the rate of increase of the 45:55-5% is 19.80% while the

45:55-25% demonstrates 719.72 %. On the other hand, a likewise trend has been shown by 50:50-25% with a 597.42 % improvement in comparison to the base bitumen.

Table 4.18: Rotational viscosity rate of increase of modified bitumens 45:55

Blend type	Rate of increase (unaged)		Rate of increase (aged)	
	135 °C	165 °C	135 °C	165 °C
Base	-	-	-	-
45:55-5%	19.80	8.06	16.56	18.55
45:55-10%	88.17	70.98	97.58	54.47
45:55-15%	215.08	192.58	204.10	198.89
45:55-20%	363.87	296.52	308.69	330.43
45:55-25%	719.72	831.25	557.27	554.70

Table 4.19: Rotational viscosity rate of increase of modified bitumens 50:50

Blend type	Rate of increase (unaged)		Rate of increase (aged)	
	135 °C	165 °C	135 °C	165 °C
Base	-	-	-	-
50:50-5%	31.17	32.11	21.05	25.98
50:50-10%	120.78	121.65	139.74	135.52
50:50-15%	292.72	256.19	248.53	257.61
50:50-20%	396.50	483.37	586.51	533.68
50:50-25%	597.42	880.20	892.57	769.31

Additionally, the temperature and the viscosity relationship are important to evaluate the bitumen mixing and the compaction temperatures. The viscosity of the bitumen is mainly associated with pumping and mixing at the hot mix plant. The higher the viscosity of the bitumen the higher will be the mixing and the compaction temperature and vice versa. Whereas lower viscosity leads to the rutting of the pavements. The mixing and the compaction temperatures of the MWCOG-45:55 and MWCOG-50:50 are provided in Table 4.20 while Figure 4.12 and Figure 4.13 depicts the temperatures at corresponding viscosities of 0.28 ± 0.02 and 0.17 ± 0.03 respectively. The mixing and the compaction temperatures of the MWCOG have followed the general trend of improvement in increasing the content of MWCOG (5%–25%). It can be seen from

Figure 4.12 and Figure 4.13 that the mixing and compaction temperature of the base bitumen is 160 °C and 145 °C respectively. However, the incorporation of the MWCOG-45:55 and MWCOG-50:50 has significantly increased the temperature. For instance, the 45:55-15% and 50:50-15% have mixing temperatures of 181°C and 180°C respectively. Moreover, a higher content of MWCOG is unfavourable as it necessitates elevated mixing and compaction temperatures for asphalt mixture preparation, which is not sustainable. The higher variation between the viscosity-temperature relationship of modified bitumen reflects the increase in the mixing and the compaction temperatures. Also, Table 4.20 presents the rate of increase (%) which further validates the temperature increase of all modified bitumen in comparison to that of the base bitumen.

Table 4.20: Mixing and compaction temperatures of modified bitumens

Blend type	Mixing temperature °C	Compaction temperature °C	Rate of increase (%)	
			Mixing temperature °C	Compaction temperature °C
Base	160	145	-	-
45:55-5%	163	150	1.87	3.45
45:55-10%	173	163	8.12	12.41
45:55-15%	181	174	13.12	20.00
45:55-20%	191	182	19.37	25.52
45:55-25%	>200	195	25.0	34.48
50:50-5%	166	154	3.75	6.21
50:50-10%	180	164	12.5	13.10
50:50-15%	192	168	18.12	22.76
50:50-20%	>200	180	22.5	30.34
50:50-25%	>200	>200	25.0	34.48

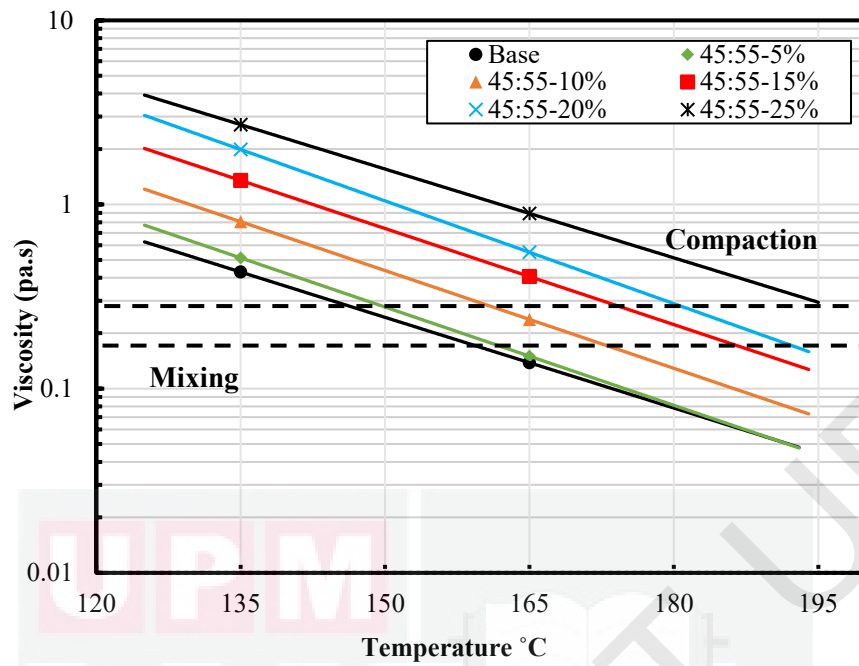


Figure 4.12: Mixing and compaction temperature of 45:50 modified bitumens

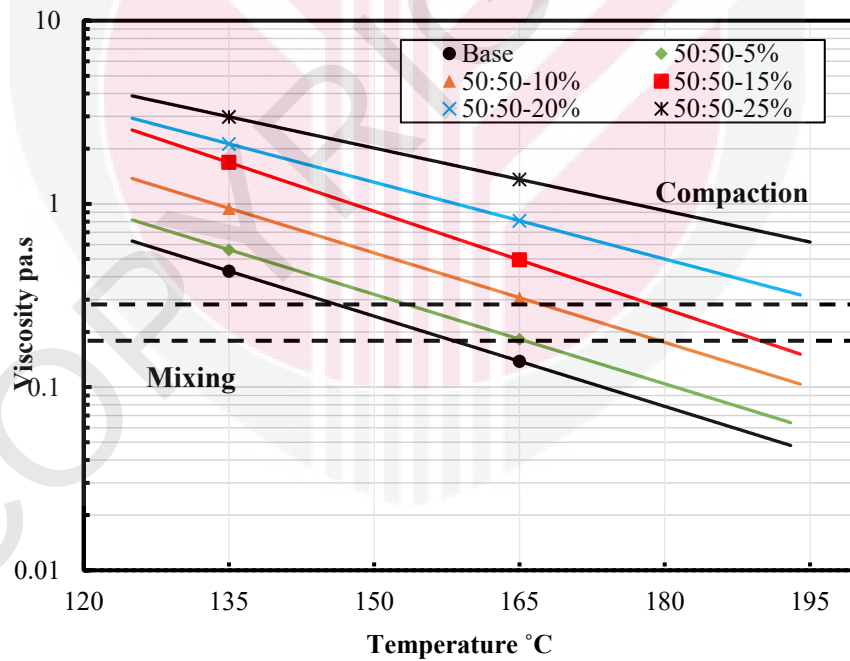


Figure 4.13: Mixing and compaction temperature of 50:50 modified bitumens

Figure 4.14 depicts the effect of the MWCOG on the mixing and compaction temperatures of the MWCOG-45:55 and MWCOG-50:50 modified. It can be observed

that the increasing content of the MWCOG significantly increases the desirable temperatures. However, MWCOG-50:50 demonstrated higher mixing temperatures, attributed to the high percentage of SBS compared to MWCOG-45:55 in the composite material. As probable, SBS imparts stiffening characteristics to bitumen, thereby increasing the viscosity of the modified bitumen and consequently requiring higher mixing temperatures. A higher content of MWCOG is unfavourable for bitumen modification as it elevates temperatures. Hence, the optimal percentage of 15% represents the maximum limit; beyond this, asphalt mixture preparation becomes unsustainable and less effective. Furthermore, the slope (%) of MWCOG-45:55 and MWCOG-50:50 are provided in Table 4.21. The 45:55-5% and 50:50-5% at a temperature of 135 °C demonstrate a slope of 1.66 % and 2.65 % respectively. It shows that the 50:50 is higher in mixing temperature compared to the 45:55. Similarly, the 45:55-25% and 50:50-25% have shown an increase in slope (%) with values of 9.13% and 10.23% respectively. Therefore, it is concluded that the increase in slope is caused by the increase in MWCOG content and vice versa.

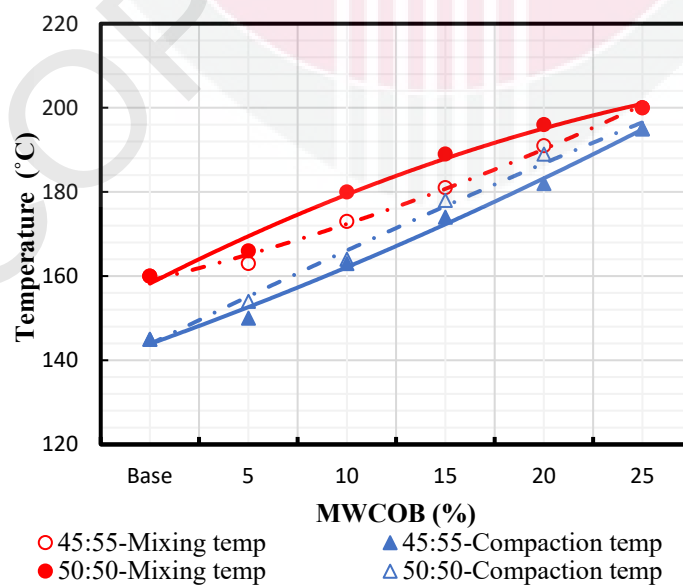


Figure 4.14: Effect of modified WCO on mixing and compaction temperatures

Table 4.21: Slope of 45:55 and 50:50 modified bitumen

Blend type	Slope (Pa.s/ °C)	
	135 °C	165 °C
Base	-	-
50:50-5%	1.66	0.23
50:50-10%	3.76	0.99
50:50-15%	6.14	1.78
50:50-20%	7.79	2.06
50:50-25%	9.13	3.02
50:50-5%	2.65	0.89
50:50-10%	5.17	1.69
50:50-15%	8.35	2.37
50:50-20%	8.49	3.36
50:50-25%	10.23	4.89

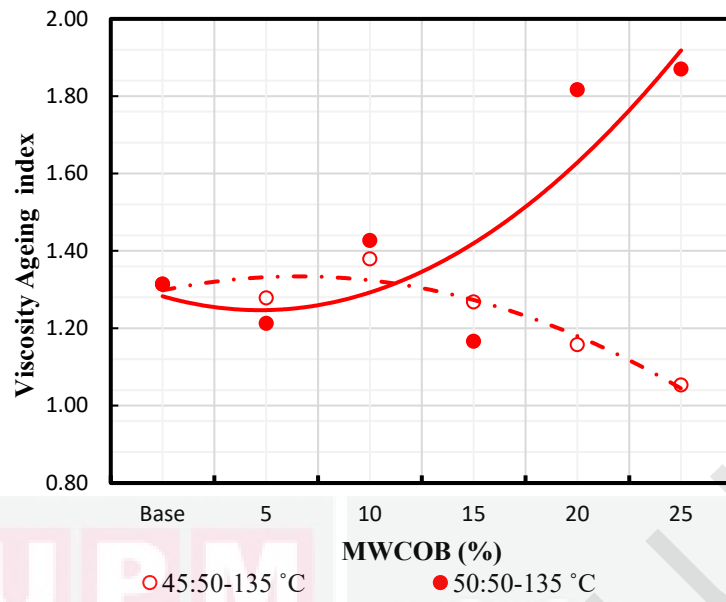
4.5.2 Ageing indices of modified bitumens

The ageing of the bitumens and the modified bitumens are complex phenomena mainly dependent on many factors such as environmental, mechanical and chemical changes and ultimately affect the long-term service applications. The ageing index is usually used for intricate changes in the properties of the bitumen over time and is important for predicting and assessing the performance and durability of the bitumen. The viscosity variations in bitumen correspond to the changes in rheological properties and molecular structure. Nevertheless, measuring viscosity both before and after ageing is a crucial indicator of bitumen durability, providing insights into its suitability for various applications. Thus, the base and the MWCOG-45:55 and MWCOG-50:50 modified bitumen ageing indices were determined using the equation (3.1). The results of all modified bitumen ageing indices are provided in Table 4.22 and depicted in Figure 4.15.

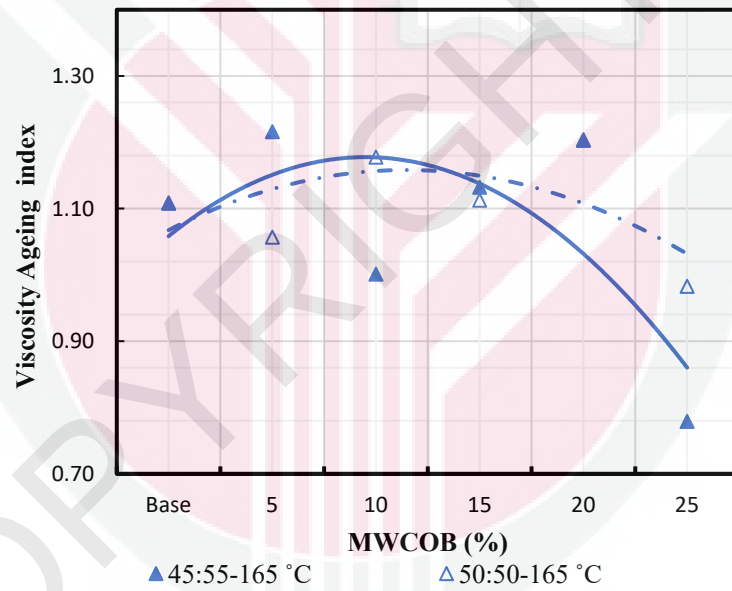
Table 4.22: Viscosity ageing indices of modified bitumens

Blend type	Viscosity ageing indices		Rate of increase (%)	
	135 °C	165 °C	135 °C	165 °C
Base	1.314	1.108	-	-
45:55-5%	1.278	1.216	-2.70	9.71
45:55-10%	1.379	1.001	5.00	-9.66
45:55-15%	1.268	1.132	-3.48	2.16
45:55-20%	1.158	1.203	-11.90	8.55
45:55-25%	1.053	0.779	-19.82	-29.70
50:50-5%	1.212	1.057	-7.71	-4.64
50:50-10%	1.427	1.178	8.59	6.26
50:50-15%	1.166	1.113	-11.25	0.40
50:50-20%	1.817	1.204	38.27	8.62
50:50-25%	1.870	0.983	42.32	-11.31

The results indicate a trend where the viscosity ageing indices of the modified bitumen decrease with an increase in MWCOG content in the bitumen. The overall decreasing trend signifies an enhancement in resistance to ageing compared to the base bitumen. Nevertheless, the 50:50-20% and 50:50-25% have demonstrated the higher viscosity ageing indices of 1.817 and 1.870 at 135 °C as shown in Figure 4.15a. As expected, the higher content of the MWCOG-50:50 causes non-homogeneity and sudden change in the behaviour of modified bitumen. Moreover, the increased quantity of SBS within the composite material notably stiffens it, resulting in an unexpected rise in ageing indices (Behnood and Olek, 2017). On the other hand, the ageing indices of the MWCOG-45:55 modified bitumen at 135 °C decreased on increasing content of the MWCOG which signifies the better resistance to the ageing of bitumen. The 19.82% improvement has been noticed compared to the base bitumen. Similarly, the ageing indices results of the modified bitumen at 165 °C are illustrated in Figure 4.15b. It is summarized that on the higher temperature, the ageing indices of both modified bitumen signify the decreasing trend which corresponds to the improvement in the ageing resistance of bitumen. Thus, the overall outcomes of the modified blends are promising and have the maximum ability to resist ageing resistance.



(a)



(b)

Figure 4.15: Viscosity ageing indices of modified bitumen at (a):135 °C (b):165°C

4.5.3 Dynamic rheological properties of MWCOG modified bitumens

It is acknowledged that the bitumen has exhibited viscoelastic behaviour and was primarily influenced by loading frequency and temperature changes. The phase angle

characterises the viscoelastic behaviour of the base and modified waste cooking oil bitumen (δ) and complex modulus (G^*) before and after the process of ageing. The temperature sweep and frequency sweep tests were performed to establish base and WCO-modified bitumen behaviours at various temperatures and frequencies. In the subsequent section, the isochronal plots, master curve at 65 °C, Black space diagram, and Cole-Cole diagram will be displayed to further delve into the data.

4.5.4 Temperature sweeps of modified bitumens

The dynamic mechanical analysis (DMA) was performed using a dynamic shear rheometer (DSR) following the AASHTO T315. The Thermo scientific model Haake- Rheo-Stress1 was employed to analyse the rheology of base bitumen and MWCOG-45:55 and MWCOG-50:50 modified bitumens (5–25%) at high and intermediate temperatures. The DSR evaluates the rheological properties of bitumen by measuring the complex shear modulus G^* and phase angle δ at a specified temperature and loading frequency. The G^* of the bitumen corresponds to the resistance of the bitumen towards the oscillating deformation, while the δ reflects the lag between shear stress and shear strain. The temperature sweep was performed at a constant frequency of 1.59 Hz with a 25mm diameter parallel plate geometry with a 1mm gap and an 8mm diameter geometry with a 2mm gap for the higher temperature (40–82°C) and intermediate temperatures (10–40°C), respectively.

4.5.4.1 Isochronal Plots

The complex modulus (G^*) and phase angle (δ) isochronal plots versus temperature at a frequency of 1.59 Hz for MWCOG-45:55 and MWCOG-50:50 modified bitumen

before and after ageing are presented in Table 4.23 and Table 4.24 while illustrated in Figure 4.16 and Figure 4.17 respectively. The findings show that increasing the MWCOG content in the modified bitumen improves its temperature susceptibility. The enhancement in the temperature susceptibility is inferred by a decline in the slope of the MWCOG bitumens complex modulus isochrones.

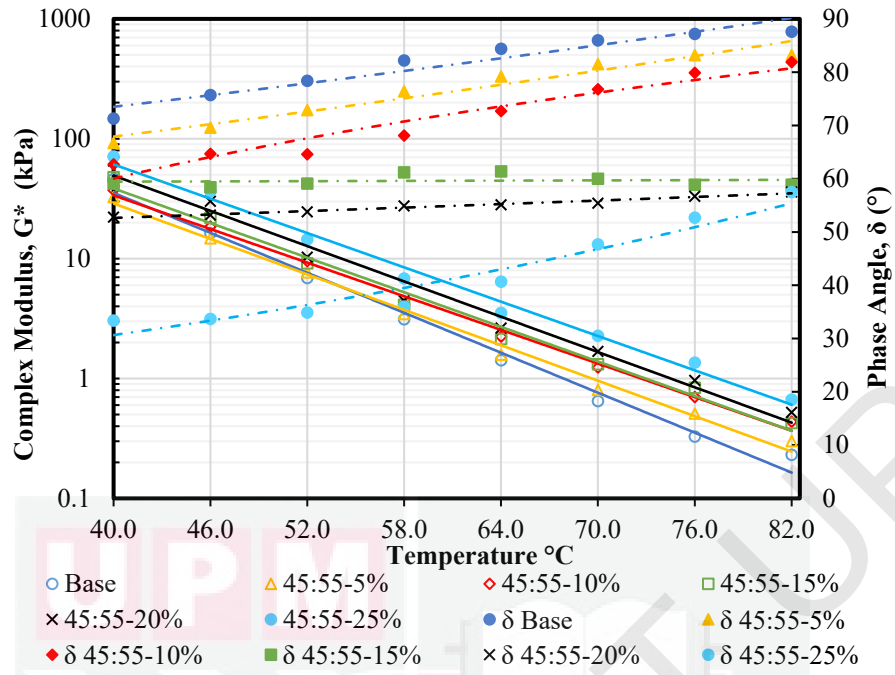
Table 4.23: Temperature sweep results of unaged base and modified bitumen at varying temperatures

Blend code	Complex modulus G^* (kPa)							
	40 °C	46 °C	52 °C	58 °C	64 °C	70 °C	76 °C	82 °C
Base	46.20	16.27	6.90	3.13	1.42	0.65	0.33	0.23
45:55-5%	32.66	14.82	7.69	3.46	1.58	0.81	0.51	0.30
45:55-10%	37.38	18.50	9.56	4.17	2.24	1.24	0.70	0.44
45:55-15%	47.83	21.92	9.17	4.13	2.14	1.32	0.84	0.43
45:55-20%	65.17	30.07	10.30	4.46	2.64	1.68	0.97	0.52
45:55-25%	71.17	36.60	14.47	6.85	3.53	2.28	1.36	0.67
50:50-5%	67.27	26.93	9.33	3.36	1.66	0.75	0.42	0.26
50:50-10%	78.30	31.53	12.11	5.92	3.63	1.72	1.08	0.71
50:50-15%	98.30	37.66	14.75	7.76	4.87	2.27	1.40	0.74
50:50-20%	103.88	47.30	16.31	8.45	5.03	2.73	1.76	0.96
50:50-25%	124.97	62.28	27.11	9.11	4.93	3.23	2.35	1.91

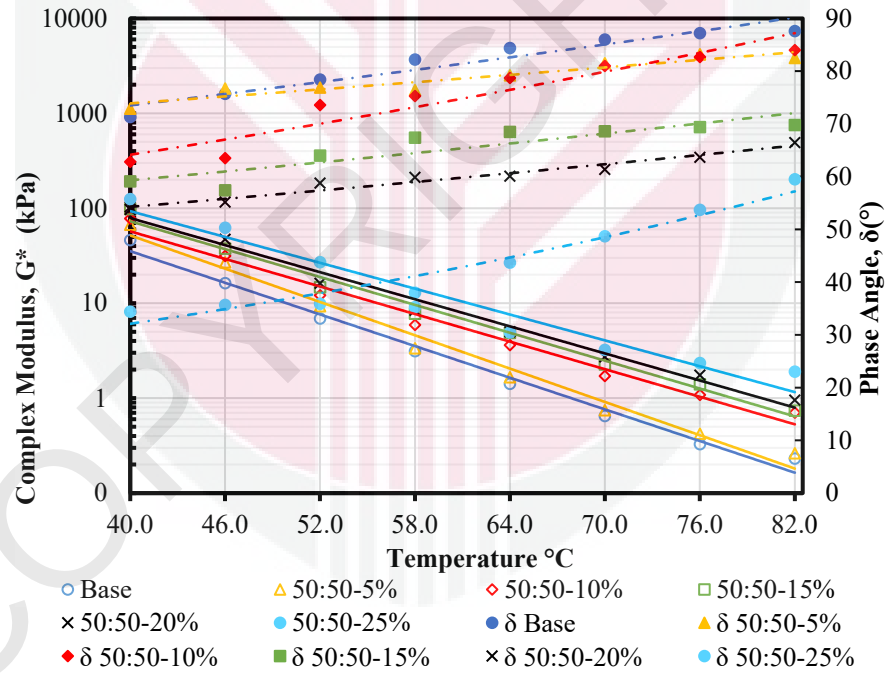
The G^* of all the MWCOG-45:55 modified bitumens are quite similar at lower temperatures except 45:55-25%. However, a similar trend has been observed for MWCOG-50:50 modified bitumen. It was observed that with an increase in temperature, the G^* is reduced gradually for the MWCOG-45:55, MWCOG-50:50 modified bitumens and base bitumen. However, the viscoelastic performance of the modified bitumens with the increasing content of MWCOG is higher than the base bitumen. However, the performance of the MWCOG-45:55 modified bitumens demonstrated a lower G^* at a temperature of 58 °C than the MWCO-50:50. This is due to the higher content of the WCO in the MWCOG-45:55 compared to the MWOCB-50:50 which has decreased the stiffness of the modified bitumens. Furthermore, the MWCOG-45:55 modified bitumens have similar G^* values as MWCOG-50:50 at

higher temperatures. It comes to an understanding that 45:55 is an optimal ratio to get comparable properties to that ratio of 50:50 at a higher temperature. As expected, the 45:55-25% and 50:50-25% have shown excessive G^* values at each desired temperature, which is attributed to weak bitumen and MWCOG compatibility.

This behaviour has been noticed by other WCO-modified bitumen with co-modifier studies (Niu et al., 2021b; Saboo et al., 2021a). The modified bitumen 45:55-15%, 50:50-10%, and 50:50-15% showed enhanced performance because of higher stiffness at 64 °C and 76 °C temperatures than base bitumen. In principle, the structure of WCO is similar to light components of bitumen; after cross-linking with SBS the MWCO is more compatible with bitumen. Also, a significant number of cross-linking reactions between WCO and SBS can occur, enhancing the three-dimensional network structure in modified bitumen (Luo et al., 2022a). Thus, improving the stability and temperature resistance of modified bitumens. However, regardless of MWCOG concentration, the G^* of 45:55-10%, 45:55-15%, 45:55-20%, 50:50-10%, 50:50-15%, and 50:50-20%, are equivalent and found as analogous at 82 °C.



(a)



(b)

Figure 4.16: Isochronal plots of complex modulus and phase angle of unaged WCO modified bitumen: (a) 45:55 (b) 50:50

Figure 4.16 displays the δ results for MWCOG-45:55 and MWCOG-50:50 modified bitumens. It is elucidated that modified bitumen has a reduced stiffness at elevated

temperatures and a higher elasticity at lower temperatures. However, the MWCOG-45:55 and MWCOG-50:50 modified bitumen have lower δ compared to base bitumen. As the MWCOG content increases, all the modified bitumens represent a continuous decreasing trend of δ ; this shows that bitumen has become more elastic. It can be noted that the δ of base bitumen at a temperature of 40 °C is 71.3° and it has increased to 87.60° at a higher temperature of 82 °C. However, for 45:55-5%, 45:55-10%, 45:55-15% the δ was decrease to 83.0°, 83.9°, and 58.9° at temperatures of 82 °C. Similarly, a substantial decrease in the δ has been observed at a temperature of 40 °C contrasted to that of base bitumen. The modified bitumens 45:55-25% and 50:50-25% have shown an enormous decrease in δ at higher temperatures. This reveals that the higher content of MWCOG began to construct a heavy cross-linking network, leading to the transfer of elasticity to bitumen (Liu et al., 2020).

Table 4.24 provides the results of the complex modulus and phase angle of the modified bitumen after the process of ageing and is also illustrated in Figure 4.17. The finding demonstrated the constant increase in complex modulus at all temperatures after the ageing of the modified bitumen. This significant increase is mainly attributed to the oxidation of the bitumen regardless of the MWCOG modification. For instance, the 45:55-5% has a G^* of 3.89 kPa at 64 °C which is increased to 10.87 kPa for 45:55-5% kPa. Similarly, 50:50-5% demonstrates the 5.15 kPa of complex modulus which is increased to 17.70 kPa at extremely high content of the MWCOG. This indicates that the MWCOG at both ratios significantly enhanced the properties. Furthermore, it is noteworthy that on lower temperatures the complex modulus of the 45:55-20%, 45:5-25%, 50:50-20% and 50:50-25% has lower values compared to the other blends which reflects the better viscoelastic behaviour of modified bitumens. However, on

increasing temperature to 70 °C and 76 °C the performance is promising and stable. This behaviour of viscoelasticity and lower temperature is due to the WCO within the bitumen matrix.

Table 4.24: Temperature sweep results of aged base and modified bitumen at varying temperatures

Blend code	Complex modulus G^* (kPa)							
	40 °C	46 °C	52 °C	58 °C	64 °C	70 °C	76 °C	82 °C
Base	88.17	36.87	17.67	7.56	3.58	1.57	0.75	0.40
45:55-5%	94.63	49.43	18.40	7.70	3.89	1.88	1.05	0.76
45:55-10%	112.33	48.73	21.67	9.33	4.55	2.83	1.73	1.06
45:55-15%	40.33	26.30	16.63	13.07	8.32	5.58	3.34	2.17
45:55-20%	34.93	20.60	12.47	7.13	4.47	3.22	2.71	1.98
45:55-25%	45.67	31.02	22.43	16.47	10.87	6.94	5.20	3.41
50:50-5%	143.33	86.07	32.45	11.03	5.15	2.73	1.41	0.71
50:50-10%	163.33	95.81	39.98	20.43	11.40	6.12	3.90	2.37
50:50-15%	197.23	58.43	33.87	24.45	15.22	9.96	5.99	3.44
50:50-20%	38.85	34.75	22.68	14.23	11.57	7.43	5.30	3.03
50:50-25%	38.40	32.40	24.47	19.33	17.70	13.67	10.47	6.18

On the other hand, the phase angle of MWCOG-45:55 and MWCOG-50:50 modified bitumen are depicted in Figure 4.17. The modified bitumen with MWCOG-45:55 demonstrates viscoelastic behaviour, indicated by trends toward lower phase angles at lower temperatures and vice versa. Conversely, the behaviour of MWCOG-50:50 is more skewed toward the elastic portion, showcasing lower δ values even at significantly higher temperatures. It can be noted that the δ of base bitumen at a temperature of 40 °C is 64.5° and it has increased to 86.70° at a higher temperature of 82 °C. However, for 45:55-5%, 45:55-10%, 45:55-15% the δ was decrease to 79.0°, 71.3°, and 66.4° at temperatures of 82 °C. Similarly, a substantial decrease in the δ has been observed at a temperature of 40 °C contrasted to that of base bitumen. The modified bitumens 45:55-25% and 50:50-25% have shown an enormous decrease in δ at lower and higher temperatures.

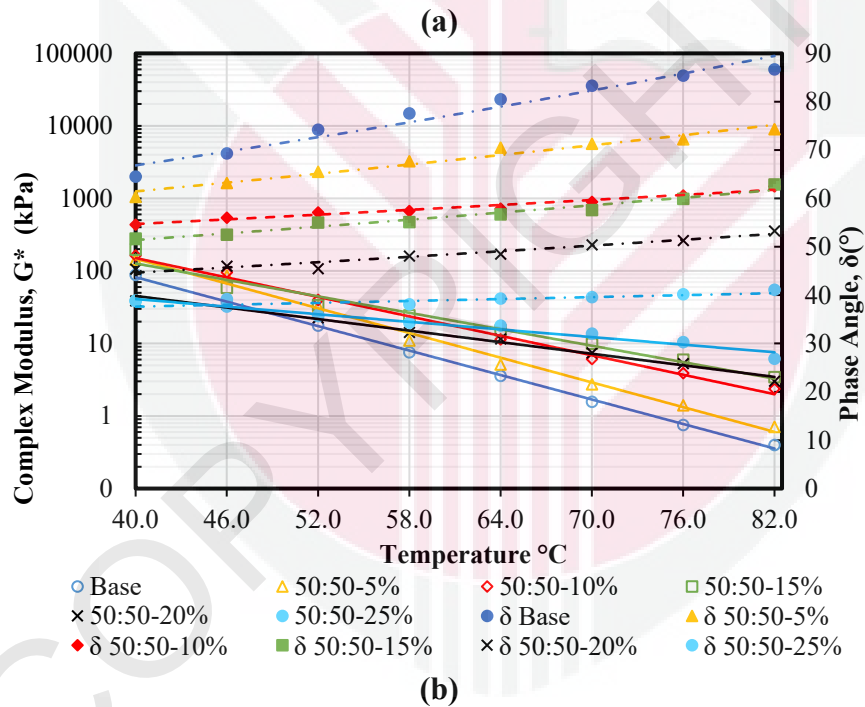
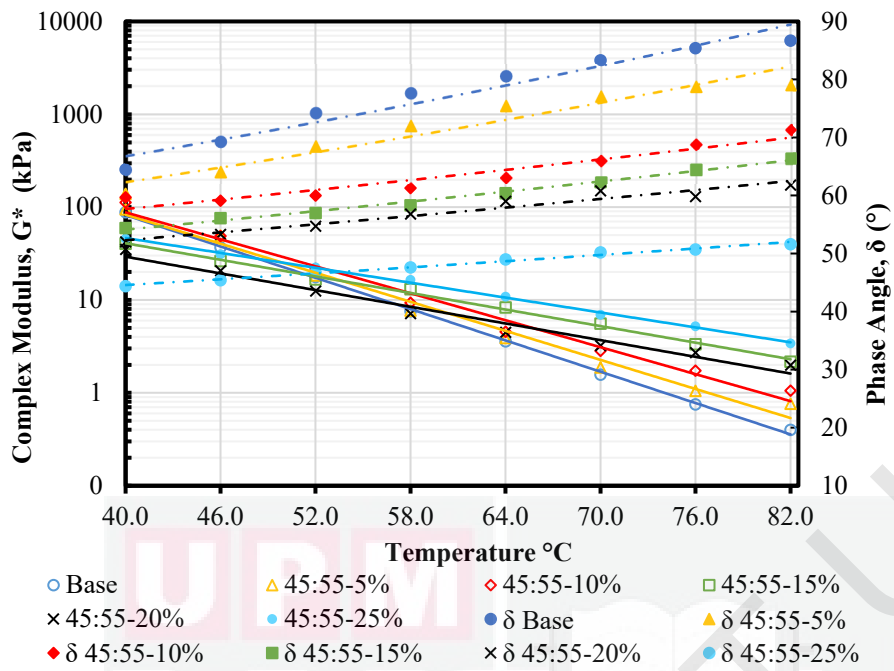


Figure 4.17: Isochronal plots of complex modulus and phase angle of aged WCO modified bitumen; (a) 45:55 (b) 50:50

4.5.4.2 Rutting parameter WCO modified bitumens

The rutting parameter ($G^*/\sin\delta$) of the MWCOG-45:55 and MWCOG-50:50 modified bitumens were evaluated at 1.59 Hz. Table 4.25 presents the results of the rutting

parameter and PG grading while Figure 4.18 illustrates the $G^*/\sin\delta$ of the base bitumen and modified bitumen at temperatures ranging from 40–82 °C. As per the super pav specifications, the $G^*/\sin\delta$ for the unaged and aged bitumen must be higher than 1000 Pa and 2200 Pa respectively to control the field rutting (Kennedy et al., 1994).

Table 4.25: Rutting parameter of all blends at 64 °C and PG grading

Blend type	Complex modulus (kPa)	$G^*/\sin(\delta)$ (kPa)	δ (°)	Failure Temperature °C	PG
Base	1.42	1.43	82.90	67.8	64
45:55-5%	1.58	1.61	79.17	68.2	64
45:55-10%	2.24	2.35	72.77	72.9	70
45:55-15%	2.14	2.44	61.5	76.0	76
45:55-20%	2.64	3.21	55.2	77.1	76
45:55-25%	3.53	5.43	40.5	80.1	76
50:50-5%	1.66	1.7	79.3	67.3	64
50:50-10%	3.63	3.7	78.6	76.3	76
50:50-15%	4.87	5.22	68.7	79.9	76
50:50-20%	5.03	5.78	60.5	82.0	82
50:50-25%	4.93	7.15	43.6	82.0	82

It can be observed from Figure 4.18 that adding MWCOG (5–25 %) to bitumen increases its rutting resistance. The 45:55-5% and 50:50-5% modified bitumens have shown likewise performance as base bitumen with a performance temperature of 67.9 °C, 68.7 °C, and 65.9 °C, respectively. The increasing dosage of the MWCOG demonstrated a reiterated likewise trend. Hence, 45:55-10%, 45:55-15%, 45:55-20%, 50:50-10%, and 50:50-15% have improved the performance grade and have satisfied the criterion at 66.2 °C, 76.2 °C, 77.9 °C, 76.2 °C, and 78.7 °C, respectively. Conversely, the modified bitumen 45:55-25%, 50:50-20% and 50:50-25% have illustrated the infinite $G^*/\sin\delta$ performance. This extraneous data result is caused by the higher MWCOG concentration, which conclusively dominates the modified bitumen properties. Moreover, the performance of modified bitumens may be affected by incompatibility and poor storage stability at higher MWCOG concentrations, and

similar modification trends have been reported in the literature (Liu et al., 2020; Luo et al., 2017).

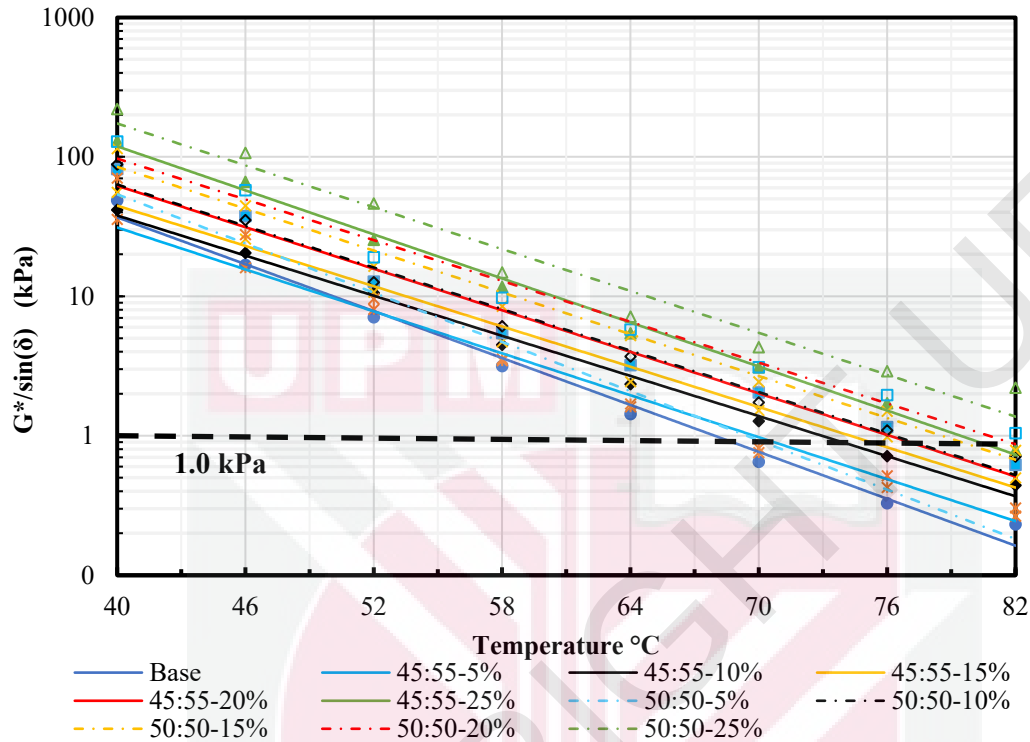


Figure 4.18: Temperature effect on rutting parameter ($G^*/\sin \delta$) of 45:55 and 50:50 unaged blends

Furthermore, the increasing content of the MWCOG substantially modified the base bitumen and improved the failure temperatures as shown in Figure 4.19. The failure temperature of the base bitumen is 67.8 °C whereas the 45:55-10% and 50:50-10% demonstrated an improved failure temperature of 72.9 °C and 76.3 °C respectively. It is noteworthy that the performance grading of the base bitumen is improved from 64 °C to 76 °C whilst adding the 10% of MWCOG-50:50. The MWCOG-45:55 has demonstrated a maximum of PG76 however the MWCOG-50:50 has achieved the PG82 even at a 20% incorporation of MWCOG. Moreover, similar trends have been observed in the enhancement of the $G^*/\sin \delta$ at varying contents for the MWCOG-45:55

and MWCOG-50:50 at 64 °C as presented in Figure 4.20. These results imply that the incorporation of the MWCOG significantly enhances the rutting resistance of the modified bitumens. However, the 45:55-25% and 50:50-25% have shown higher rutting values compared to the base and all other modified bitumen. The lower stiffness of the 45:55 modified bitumen is owing to its higher WCO content within the bitumen matrix.

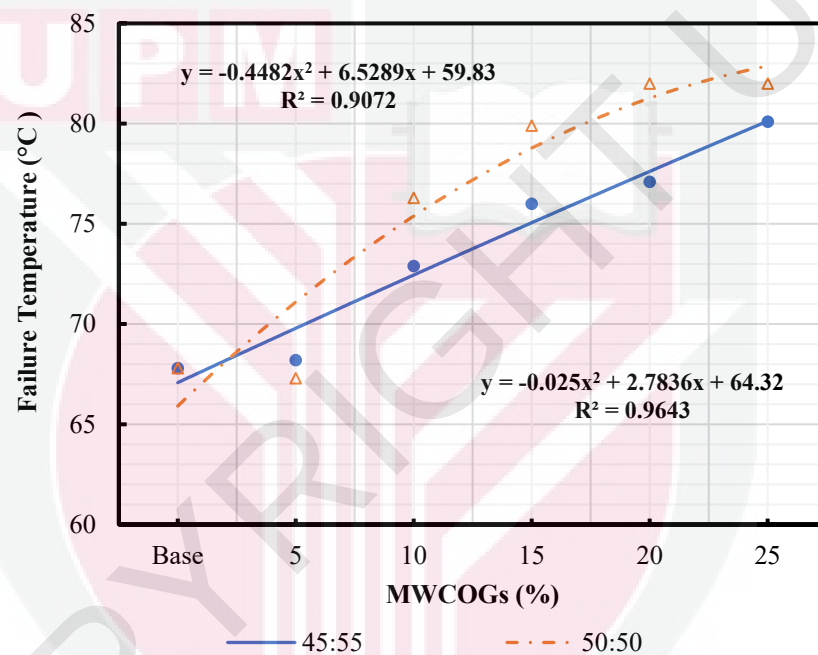


Figure 4.19: Effect of MWCOG on the failure temperatures of unaged modified bitumens

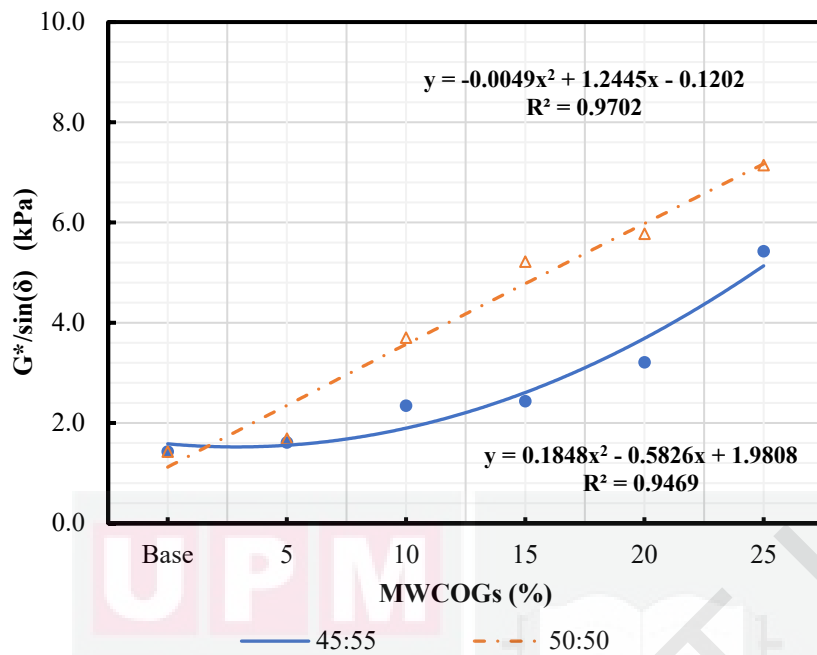


Figure 4.20: Effect of MWCOG on a rutting parameter of unaged modified bitumens at 64 °C

Figure 4.21 illustrates the RTFO aged modified and base bitumen results in a temperature range of 40-82 °C. The oxidative ageing further increased the stiffness and the rutting parameter of the modified bitumens. The rutting parameter of 2200 Pa is an allowable limit of the bitumen and the modified bitumen after the process of short-term ageing. The results after the short-term process of ageing are consistent with the unaged results of the modified bitumens. Whereas the 45:55-25%, 50:50-20% and 50:50-20% have a rutting parameter beyond the temperature of 82 °C. The 45:55-5% modified bitumens have shown similar performance as base bitumen with a performance failure temperature of 69.7 °C compared to that of the 67.1°C of base bitumen. The increasing content of the MWCOG 45:55 and MWCOG-50:50 demonstrated an increased trend similar to unaged modified bitumen with an improved rutting parameter. Therefore, 45:55-10%, 45:55-15%, 45:55-20%, 50:50-10%, and 50:50-15% have improved the performance grade and have satisfied the criterion at

73.9 °C, 82.0 °C, 76.2 °C, 81.0 °C, and 82.0 °C, respectively. On the contrary, the modified bitumen 45:55-25%, 50:50-20% and 50:50-25% have illustrated the infinite $G^*/\sin\delta$ performance. This extraneous data result is caused by the higher MWCOG concentration, which conclusively dominates the modified bitumen properties. Moreover, the performance of modified bitumens may be affected by incompatibility and poor storage stability at higher MWCOG concentrations, and similar modification trends have been reported in the literature (Liu et al., 2020; Luo et al., 2017).

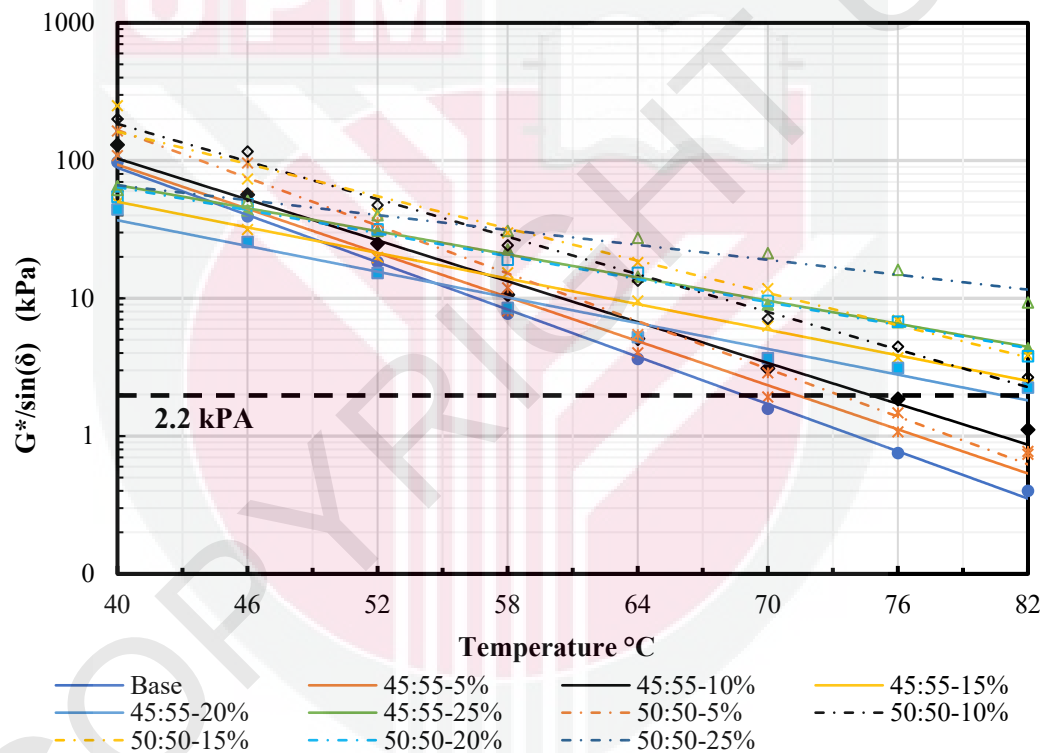


Figure 4.21: Temperature effect on rutting parameter ($G^*/\sin \delta$) of 45:55 and 50:50 aged blends

Table 4.26 provides a comparative assessment of the unaged and aged rutting parameters rate of increase and rate and Figure 4.22 depicts the effect of the increasing content of the MWCOG on the rutting resistance of the modified bitumen in comparison to the base bitumen. For instance, the rate increase of unaged modified

bitumen, 45:55-5% is 12.6% which is increased to 279% at 45:55-25% compared to the base bitumen. Similarly, the aged bitumen 45:55-25% demonstrated a 295% improvement. The higher content of the MWCOG is not desirable therefore the optimum content of up to 15 % is promising for optimum performance of bitumens.

Table 4.26: Rutting rate of increase of unaged and aged blends at 64 °C

Blend type	Failure Temperature °C	Rate of increase (%)	
		G*/sin(δ) (kPa) (Unaged)	G*/sin(δ) (kPa) (Aged)
Base	-	-	-
45:55-5%	0.6	12.6	10.8
45:55-10%	7.5	64.3	40.3
45:55-15%	12.1	70.6	163.7
45:55-20%	13.7	124.5	43.8
45:55-25%	18.1	279.7	295.2
50:50-5%	-0.7	18.9	50.4
50:50-10%	12.5	158.7	270.0
50:50-15%	17.8	265.0	401.5
50:50-20%	20.9	304.2	321.5
50:50-25%	20.9	400.0	658.2

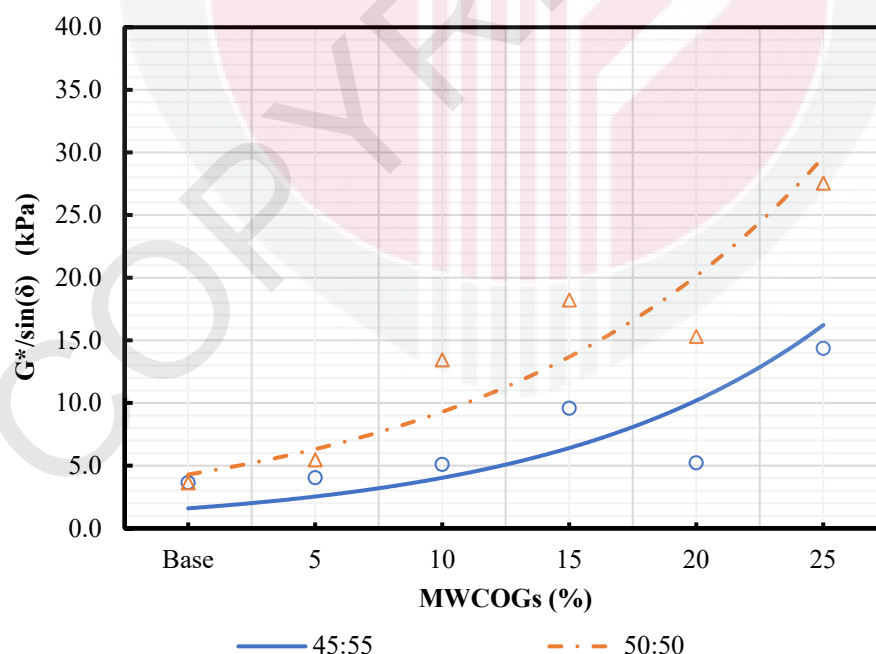


Figure 4.22: Effect of MWCOG on rutting parameter of aged modified bitumens at 64 °C

4.5.4.3 Fatigue parameter

In addition to rutting, intermediate temperature fatigue cracking causes significant distress. The most common cause of microdamage in pavements is fatigue damage, which develops in the bitumen mastic due to repetitive loads (Qian et al., 2019). According to super pave regulation, the maximum limit should not exceed 5000 kPa for PAV-aged bitumen, indicating the bitumen's capability to withstand cracking at an intermediate temperature (Kennedy et al., 1994). Table 4.27 displays the fatigue parameter results of modified bitumen at varying temperatures of 10 °C–40 °C while illustrated in Figure 4.23.

Table 4.27: Temperature sweep results of PAV aged base and modified bitumen at varying intermediate temperatures

Blend code	Fatigue parameter (kPa)					
	10 °C	16 °C	22 °C	28 °C	34 °C	40 °C
Base	6567	5950	5322	3200	2102	1013
45:55-5%	4800	4210	3200	2534	2100	1250
45:55-10%	3269	2900	2650	2250	1750	950
45:55-15%	2652	2022	1725	1226	789	442
45:55-20%	1865	1490	1150	736	325	195
45:55-25%	1487	1247	994	436	145	82
50:50-5%	5325	4321	3620	2910	2113	1401
50:50-10%	3845	3225	2782	2412	1925	1043
50:50-15%	2965	2300	1987	1445	781	565
50:50-20%	2115	1832	1458	1135	465	220
50:50-25%	1895	1525	1217	725	296	123

A decrease in $G^* \sin \delta$ is correlated with a better ability of modified bitumens to resist fatigue failure and vice versa. Figure 4.23 illustrated that base and 50:50-5% modified bitumen had shown fatigue failure at 22 °C and 13 °C, respectively. Whereas the 45:55-5% has shown more improvement and failed at 11°C. In addition, all other bitumens have shown fatigue parameter values less than 5000 kPa. This demonstrates that adding WCO has supplemented the light components to the bitumen which

subsequently softened the modified bitumen and led to enhanced fatigue resistance at an intermediate temperature. The MWCOG enhanced the three-dimensional network structure in the modified bitumen, thus decreasing the cracking of bitumen due to the elastic nature of SBS (Luo et al., 2022a).

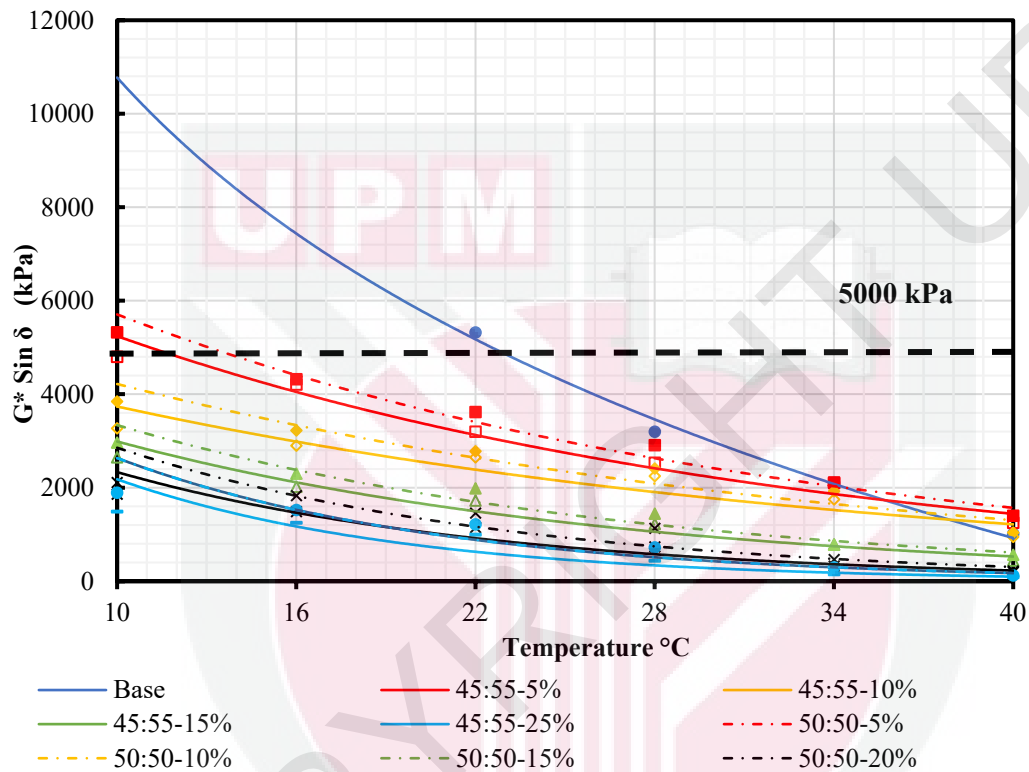


Figure 4.23: Temperature effect on fatigue parameter ($G^* \cdot \sin \delta$) of MWCOG

Furthermore, the fatigue parameter at 16 °C with a rate of decrease is presented in Table 4.28 and depicted in Figure 4.24. It can be elucidated that the increasing MWCOG content in the bitumen significantly enhances the fatigue parameters. The 45:55-5% and 45:55-25% have shown 29% and 79% improvement compared to base bitumen respectively. However, the rate of increase of the 50:50-5% and 50:50-25% is 27.8% and 74.37% respectively. The performance of the MWCOG-50:50 modified bitumens is comparatively low compared to the MWCOG-45:55 modified bitumens.

The behaviour is mainly due to the percentage variation of the WCO within the composite material. The results are consistent with the earlier discussed rutting properties and rotational viscosity.

Table 4.28: Fatigue parameters of base and modified bitumens at 16 °C

Blend type	Fatigue parameter @ 16 °C	Rate of decrease (%)
Base	5950	-
45:55-5%	4210	-29.24
45:55-10%	2900	-51.26
45:55-15%	2022	-66.02
45:55-20%	1490	-74.96
45:55-25%	1247	-79.04
50:50-5%	4321	-27.38
50:50-10%	3225	-45.80
50:50-15%	2300	-61.34
50:50-20%	1832	-69.21
50:50-25%	1525	-74.37

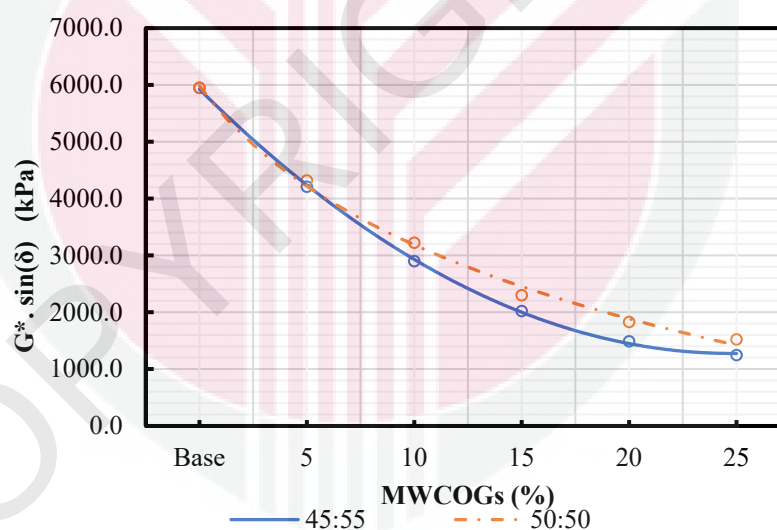


Figure 4.24: Effect of WCOBs on fatigue parameter of modified bitumens at 16 °C

4.5.5 Frequency sweep of MWCOG modified bitumens

A frequency sweep test was conducted for the original and RTFO aged MWCOG modified bitumens at 35–85 °C with 10 °C of the interval with a frequency range of

0.1 Hz to 14 Hz within the bitumen linear viscoelastic (LVE) response. The results obtained from the frequency sweep were further employed to generate master curves, Cole-Cole plots, and a Black space diagram.

4.5.5.1 Frequency sweep isochronal plots

The data acquired from the frequency sweep test is used to represent the complex modulus (G^*) and the phase angle (δ) in the form of isochronal plots. This representation is valuable for comprehending bitumen behaviour across different frequencies and temperatures. The findings from the frequency sweep, encompassing minimum and maximum frequencies, across temperatures ranging from 35 °C to 85 °C for G^* and δ , are outlined in Table 4.29 and Table 4.30 respectively. The lower frequency reflects the viscoelastic behaviour of the bitumen and the modified bitumen at slow traffic conditions and higher temperatures. Conversely, the higher frequency reflects the fast-moving traffic at intermediate temperature conditions. The results at minimum and maximum frequencies showcase the comparison and improvement among all the modified bitumen. For instance, the base bitumen at 65 °C demonstrated a complex modulus of 0.09 kPa and 9.15 kPa at frequencies of 0.10 and 14 Hz respectively. However, the 45-55-5% and 50:50-5% have shown a G^* of 0.19-15.60 kPa and 0.19-12.80 kPa respectively. It can be elucidated that the incorporation of the MWCOG enhanced the stiffness of the bitumen compared to the base bitumen.

Table 4.29: Complex modulus (kPa) results of 45:55 and 50:50 modified bitumen at 0.10 Hz and 13 Hz

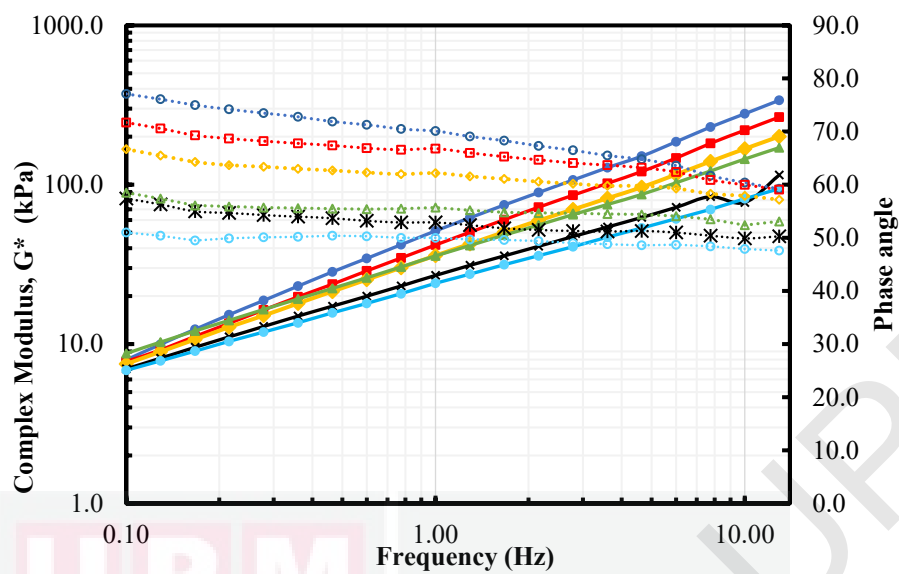
Blend type	Temperature °C											
	35 °C			45 °C			55 °C			75 °C		
	Frequency (Hz)			Frequency (Hz)			Frequency (Hz)			Frequency (Hz)		
	0.10	14		0.10	14		0.10	14		0.10	14	
Base	7.90	339		1.60	103		0.30	30.7		0.09	9.15	
45:55-5%	7.79	266		2.46	101		0.64	35.30		0.19	15.60	
45:55-10%	7.51	201		2.45	78.70		0.83	32.30		0.31	15.60	
45:55-15%	8.73	171		8.60	138		6.88	140		0.35	8.23	
45:55-20%	7.0	115		2.42	46.6		0.96	21.70		0.49	10.30	
45:55-25%	6.9	94.5		3.0	43.2		1.47	21.20		0.87	10.80	
50:50-5%	10.30	344		2.11	94.8		0.54	40.40		0.19	12.80	
50:50-10%	8.20	215		2.64	77.8		0.82	31.20		0.26	13.30	
50:50-15%	7.42	125		3.07	55.40		1.28	27.0		0.51	12.40	
50:50-20%	12.50	188		5.39	96.50		2.55	48.30		1.20	29.30	
50:50-25%	10.40	124		6.10	66.80		2.98	38.60		1.82	23.30	

Table 4.30: Phase angle results of 45:55 and 50:50 modified bitumen at 0.10 Hz and 13 Hz

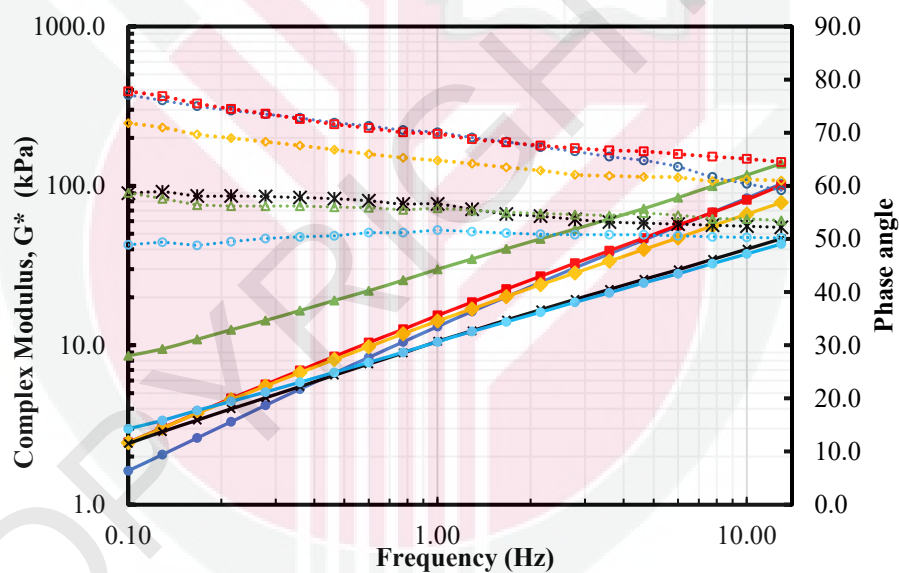
Blend type	Temperature °C											
	35 °C			45 °C			55 °C			75 °C		
	Frequency (Hz)			Frequency (Hz)			Frequency (Hz)			Frequency (Hz)		
	0.10	14		0.10	14		0.10	14		0.10	14	
Base	77.10	59.20		83.00	68.40		86.20	75.00		87.50	79.50	
45:55-5%	71.70	59.10		77.80	64.50		83.20	67.80		85.50	70.90	
45:55-10%	66.70	57.20		71.80	61.00		74.70	63.20		75.20	66.00	
45:55-15%	58.50	53.10		58.70	53.50		59.30	53.60		49.30	61.10	
45:55-20%	57.40	50.30		58.60	52.20		54.40	55.00		46.50	58.40	
45:55-25%	51.00	47.60		48.90	50.20		45.00	52.10		38.90	52.70	
50:50-5%	71.70	57.40		78.70	65.00		82.40	68.10		84.90	72.80	
50:50-10%	66.20	56.50		71.70	60.80		75.20	62.80		75.40	66.70	
50:50-15%	55.50	51.40		57.70	53.90		60.00	55.70		55.20	58.60	
50:50-20%	55.30	48.00		57.70	49.70		56.80	51.50		53.90	53.60	
50:50-25%	48.80	44.40		48.80	46.90		46.10	48.30		41.10	49.80	

However, the δ with lower values on higher frequencies is desirable. The lower values correspond to the more elastic behavior of the bitumen whereas the higher values correspond to viscous behavior. It can be seen from the results that the phase angle at a lower and higher frequency is continuously decreasing with increasing frequency (Table 4.30). The δ of the base bitumen at a frequency of 0.10 and 13 Hz are 87.50 and 79.50 respectively. Whereas the modification of the bitumen with MWCOG significantly causes the reduction of δ . The 45-55-15% and 50:50-15% improve the δ to 49.30-61.10 and 55.20-58.60 respectively. The decrease in the δ demonstrates the bitumen's better viscoelastic behaviour whereas the MWCOG-50:50 is promising in performance compared to MWCOG-45:55.

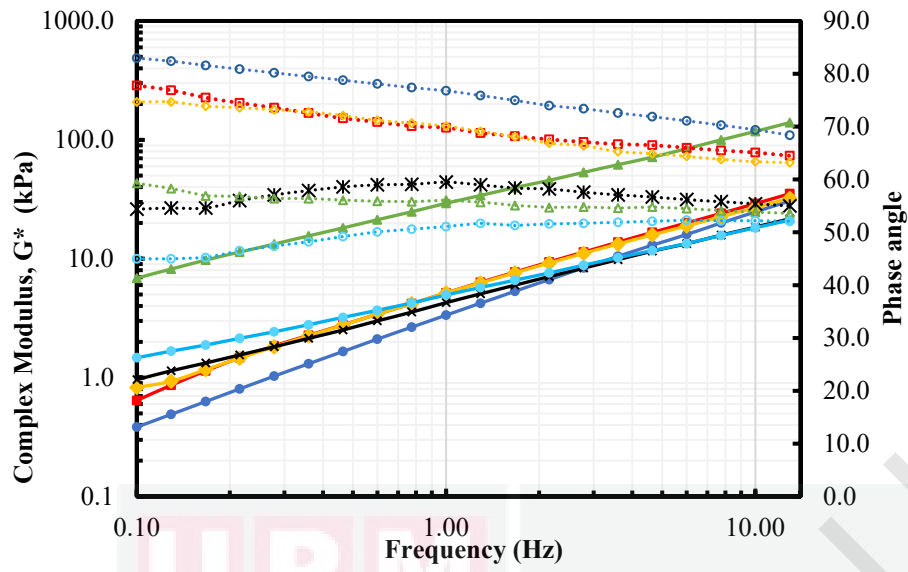
Figure 4.25 illustrates the variations in complex modulus and phase angle of unaged MWCOG-45:55 modified bitumens across a temperature range of 35°C to 80°C, extending over frequencies from 0.1 Hz to 14 Hz. The stiffness of the modified bitumen is enhanced with the increasing of the testing frequency as shown in Figure 4.25. The bitumen modification in frequency sweep plots is deemed consistent with the temperature sweep data on incorporating the MWCOG (5-25%). Conversely, the phase angle exhibited a significant reduction at all temperatures while increasing the frequency and percentage incorporation of the MWCOG. As expected, the 45:55-25% and 50:50-25% have a higher content of the MWCOG which ultimately stiffens the bitumen and causes a reduction in the δ . Similar behaviours have been observed in the earlier discussed temperature sweep results of modified bitumens. Furthermore, the results of the RTFO aged MWCOG-45:55 and MWCOG-50:50 demonstrated a likewise improvement in the complex modulus and the phase angle with higher values.



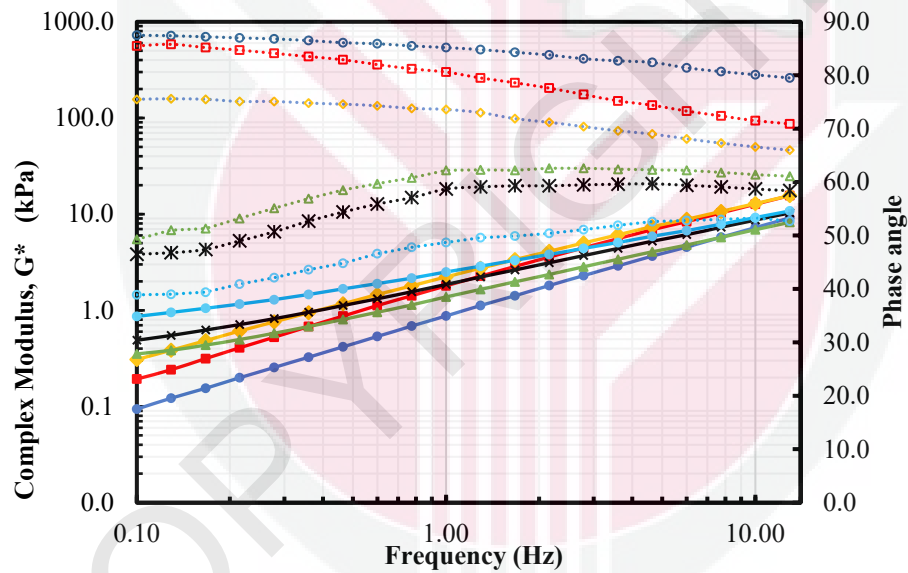
(a)



(b)



(c)



(d)

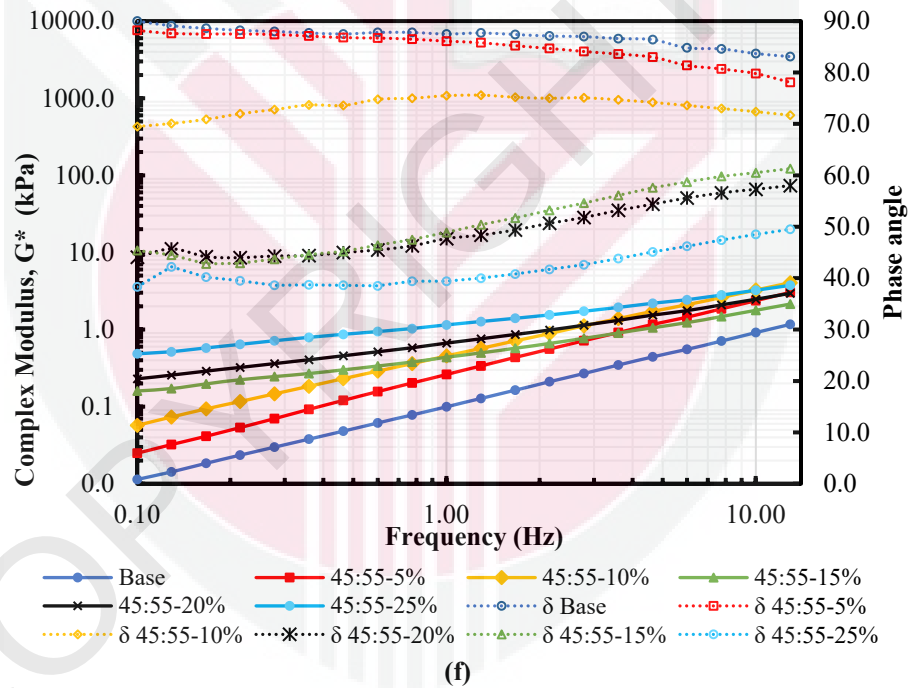
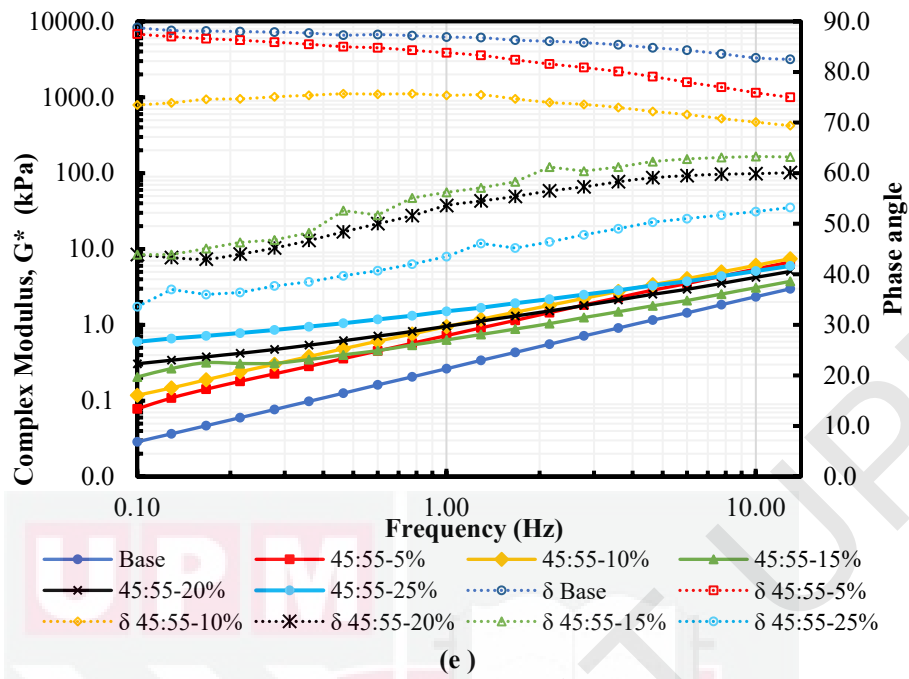


Figure 4.25: Frequency plots of unaged 45:55 modified bitumens at (a) 35 °C, (b) 45 °C, (c) 55 °C, (d) 65 °C, (e) 75 °C, (f) 85 °C

4.5.5.2 Black space diagram

The Black space diagram visually represents the unprocessed rheological data obtained from the frequency sweep test conducted between temperatures of 35°C and

85°C. It is a representation to evaluate the fluctuations in δ concerning changes in G^* . It presents data without adjustments for temperature and frequency, displaying bitumen performance in a single graph to establish correlations without the need for data manipulation using Time-Temperature Superposition (TTSP). Figure 4.26 and Figure 4.27 depict the Black space diagram for unaged and aged MWCOG-45:55 while Figure 4.28 and Figure 4.29 represent the MWCOG-50:50 modified bitumens. It was observed that at all temperature ranges the base bitumen has the highest δ compared to all other modified bitumens. It implies a smooth curve with primarily a viscous behaviour at all testing conditions. Conversely, it is a predicted property of a polymer-modified bitumen with variations in rheological data. The Black diagram findings appear to be similar to earlier research which mentioned the shift in the Black space diagram curves when the polymers are commonly used for modification of the bitumen (Jamal and Giustozzi, 2020; Joohari and Giustozzi, 2020). It has been seen that the incorporation of the MWCOG in bitumen shifts the data of the Black space diagram towards the elastic zone i.e., the lower phase angle compared to the base curves which is more viscous.

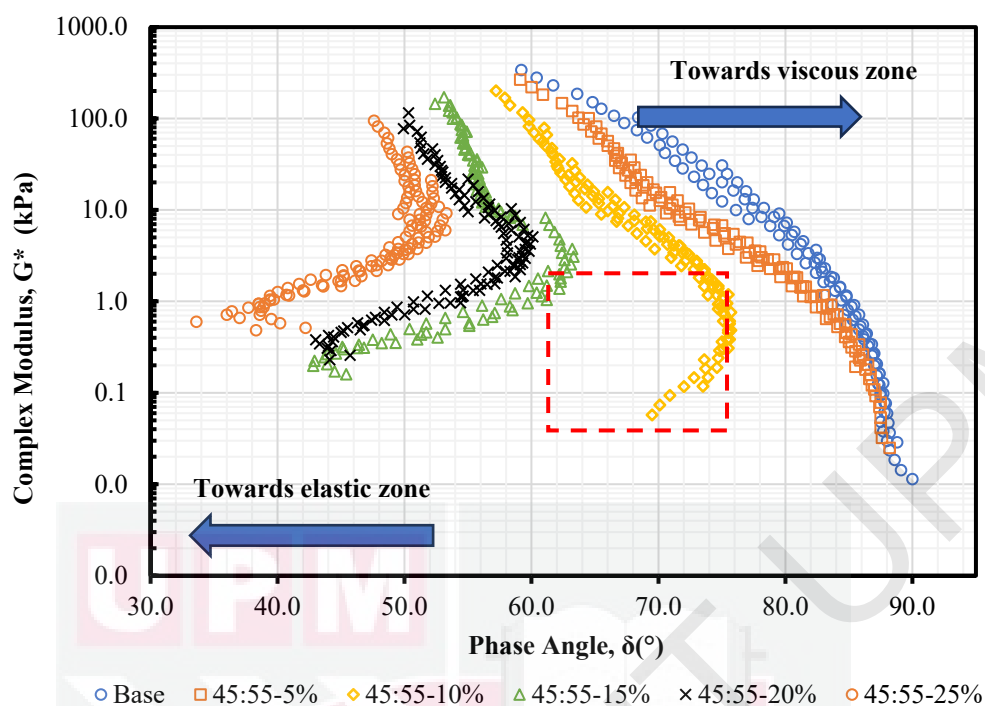


Figure 4.26: Black space diagram of unaged MWCOG-45:55 modified blends

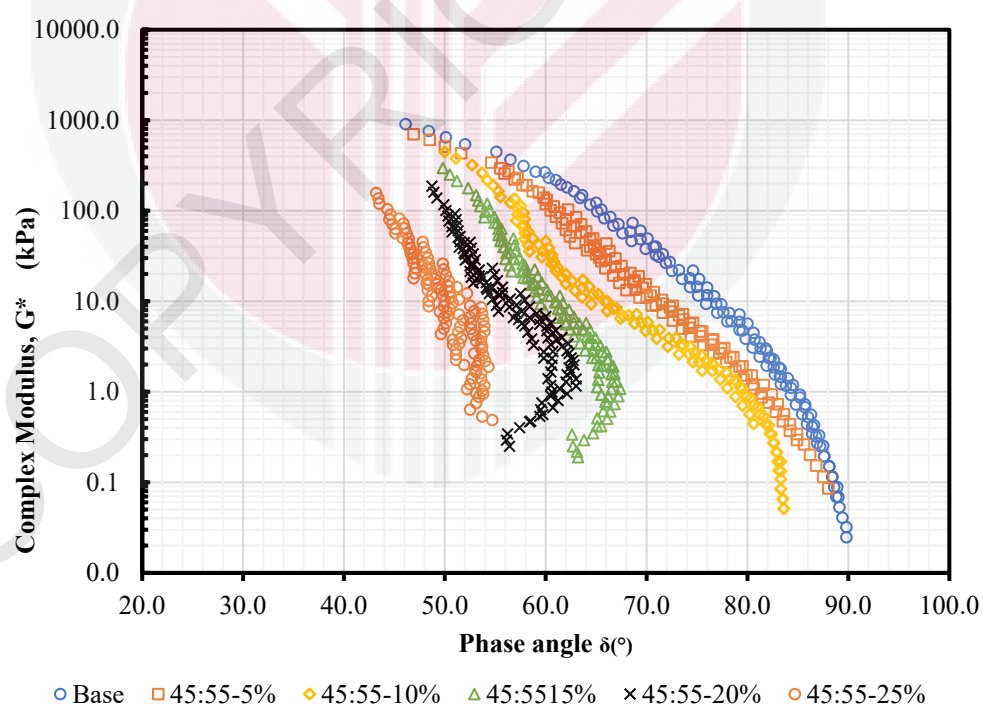


Figure 4.27: Black space diagram of RTFO aged MWCOG-45:55 modified blends

The 45:55-5% modified bitumen curves followed a similar pattern to base bitumen, slightly improving the elastic section at lower frequencies. On the other hand, the higher concentration for the 45:55-10% curve develops the wavy pattern and loses the smooth shape, and similar curves have been demonstrated by 45:55-15% and 45:55-20%. The likewise patterns are reported in earlier studies of modified bitumens (Hazoor Ansari et al., 2022; Joohari and Giustozzi, 2020). Therefore, the MWCOG influence the δ ; the 45:55-15% exhibit the lowest elasticity, followed by the 45:55-10% and 45:55-5%. The findings indicate the higher resistance against the rutting on increasing content of the MWCOG as it improves the elastic response of the bitumens. Figure 4.27 illustrates the RTFO aged Black space diagram of the MWCOG-45:55 modified bitumens. It's evident that the behaviour remains consistent with the unaged bitumen, showcasing a notable increase in complex modulus and a concurrent decrease in the phase angle for all modified bitumen samples. Therefore, the shift in rheological data towards the decreased δ is attributed to the excessive dissolution of SBS in WCO, which accelerates the cross-linking of SBS after swelling in WCO and hence improves the elastic network between base bitumen and MWCOG.

Furthermore, the efficacy of the MWCOG-50:50 on the properties of the base bitumen is assessed before and after short-term ageing as shown in Figure 4.28 and Figure 4.29. It is evident that on analysing the results of the MWCOG-50:50, the bitumen has shown a higher complex modulus compared to the MWCOG-45:55. The 50:50-5% and 50:50-10% have demonstrated a smooth curve with no disparity in the data and showing a high-temperature elastic properties. The short-term ageing of the modified bitumen has increased the complex modulus with a similar trend of the curves as unaged bitumens as shown in Figure 4.29. Moreover, the phase angle of the unaged 50:50-15% is 45.5° which is lower than the 45:55-15% of 42.8° particularly at the high temperature. As expected, the 45:55-20%, 45:55-25%, 50:50-20%, and 50:50-25%

curves exhibit trend discrepancies and are consistent with the earlier discussed results of the temperature sweep. The abrupt decrease in δ of these curves may be owing to the partial dissolution of MWCOG within bitumen due to increased concentration.

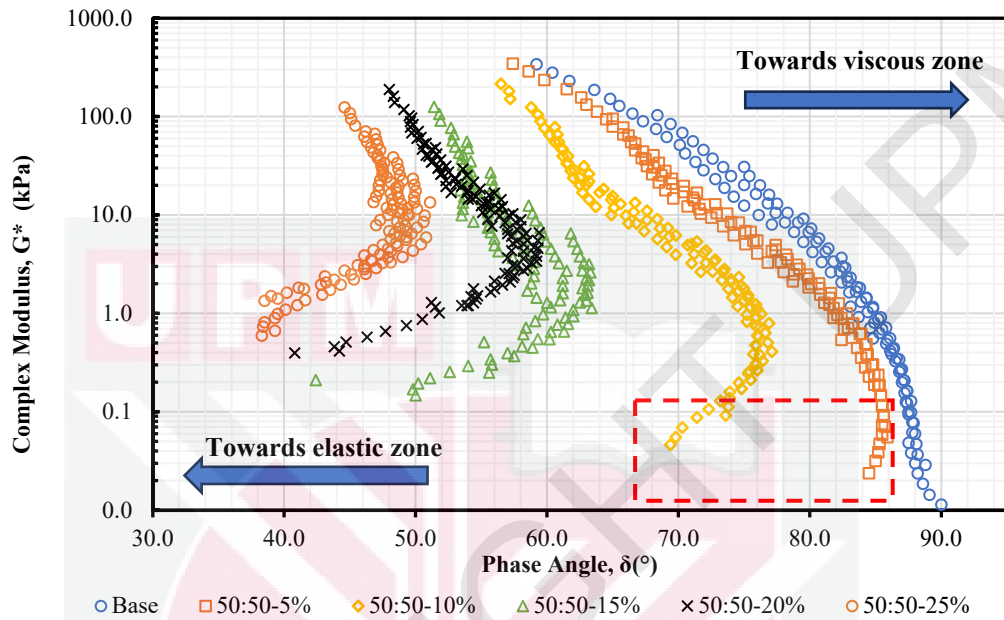


Figure 4.28: Black space diagram of unaged MWCOG-50:50 modified blends

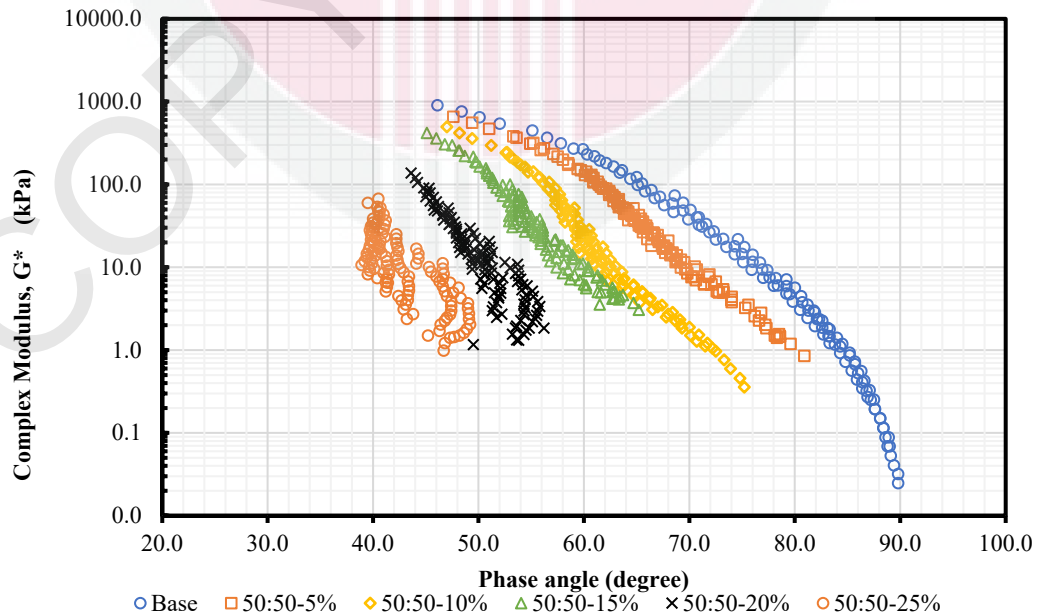


Figure 4.29: Black space diagram of aged MWCOG-50:50 modified blends

4.5.5.3 Master curve

The master curves for the MWCOG unaged and RTFO aged modified bitumens are depicted in Figure 4.30 to Figure 4.33. The curves present the complex modulus against the reduced frequency at a reference temperature of 65 °C. The WLF and sigmoidal model equation parameters for unaged and aged MWCOG-45:55 and MWCOG-50:50 are tabulated in Table 4.31 and Table 4.33. In compliance with the TTSP, higher temperatures correspond to lower frequencies and vice versa. It can be noticed that with the addition of the MWCOG (5–25%), the G^* of the modified bitumen has improved. As the reduced frequency increases the modified bitumen stiffness increases gradually.

The fitting parameters of the sigmoidal model and the WLF equation for the MWCOG-45:55 and MWCOG50:50 are provided in Table 4.31. It can be observed that the δ for all modified bitumen is negative which reflects the lower complex modulus at higher temperatures or on lower frequencies. Similar outcomes have been reported in previous studies of polymer-modified bitumens (Yusoff et al., 2013). The 45:55-15% and 50:50-20% have shown the shift of the curves towards lower complex modulus on the higher frequency or on the lower temperatures. This behaviour is desirable for the modified bitumen, particularly for the resistance against fatigue cracking. The β parameter increasing values further validate the outcomes of modification. The variation in the γ values on increasing content of the MWCOG also signifies the effect on the bitumen performance.

Table 4.31: Sigmoidal models-WLF equation parameters and coefficients for unaged bitumens

Blend type	Sigmoidal models-WLF equation parameters					
	δ	α	β	γ	C1	C2
Base	-2.53	9.97	0.20	0.38	9.87	176.18
45:55-5%	-0.17	6.8	-0.008	0.53	14.48	293.08
45:55-10%	-3.73	12.25	-0.32	0.27	20.32	299.12
45:55-15%	-2.10	2.98	0.2	1.06	21.11	107.17
45:55-20%	-5.26	17.16	0.001	0.13	6.07	126.04
45:55-25%	2.29	3.78	0.84	0.63	18.19	165.83
50:50-5%	-2.41	9.71	-0.3	0.38	11.43	210.98
50:50-10%	-1.13	8.58	-0.06	0.37	16.48	300.15
50:50-15%	-0.05	6.92	0.06	0.37	14.82	277.75
50:50-20%	-0.92	5.68	0.001	0.43	33.5	230.14
50:50-25%	-1.19	5.54	0.15	0.37	8.97	176.4

However, at lower frequencies, the MWCOG-45:55 and MWCOG-50:50 (5%, 10%, 15%) are more dominant and correlate to higher temperatures. The higher stiffness positively impacts the resistance to permanent deformation at a lower frequency. Luo et al. (2017) found a similar improvement of G^* by adding waste oil and polymer. It is inferred that adding MWCOG can improve the viscoelastic capability of modified bitumens. As anticipated, the 45:55-20%, 45:55-25%, 50:50-20% and 50:50-20% curves have indicated overlaps throughout the frequency range with other curves of modified bitumen. The behaviour could be attributed to unpredictable performance at high and low test temperatures. Table 4.32 provides the predicting equations for each modified master curve. The high R^2 values for most equations suggest that these equations provide a very good fit to the observed data, indicating their reliability in predicting the complex modulus for the corresponding bitumen blend types and percentages.

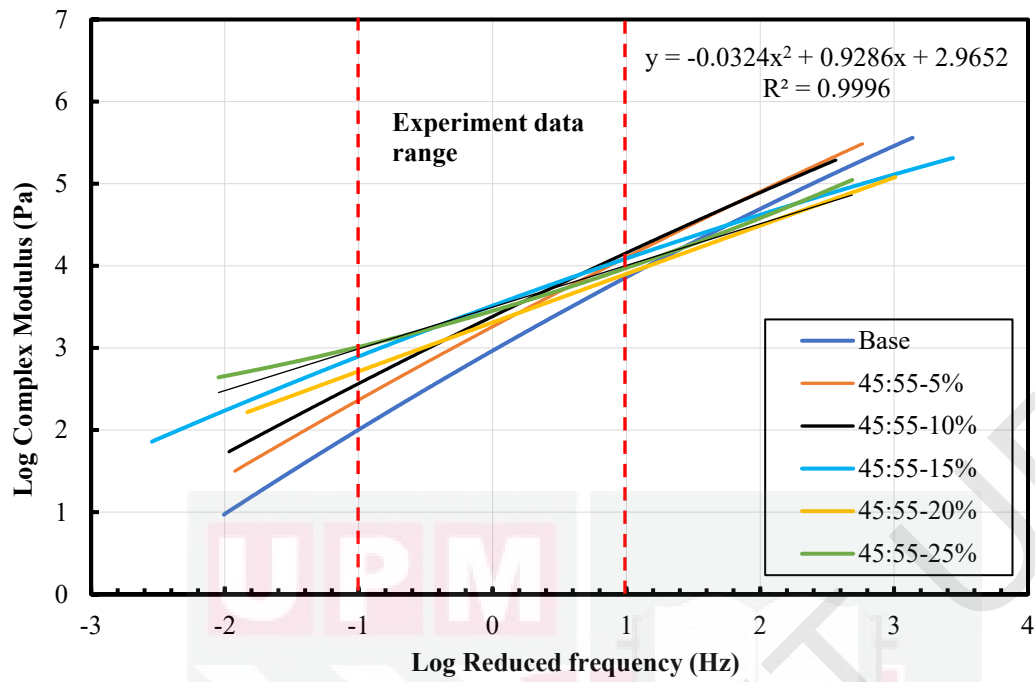


Figure 4.30: Complex modulus master curves of unaged MWCOGa-45:55 at a reference temperature of 65 °C

Table 4.32: Predicting equation of unaged MWCOG modified bitumens

Blend type	Prediction equation	R ²
Base	$y = -0.0324x^2 + 0.9286x + 2.9652$	0.99
45:55-5%	$y = -0.0228x^2 + 0.8689x + 3.258$	0.99
45:55-10%	$y = -0.0205x^2 + 0.7956x + 3.3824$	0.99
45:55-15%	$y = -0.0212x^2 + 0.5962x + 3.513$	0.97
45:55-20%	$y = -0.0016x^2 + 0.593x + 3.3092$	1
45:55-25%	$y = 0.042x^2 + 0.4809x + 3.4505$	0.99
50:50-5%	$y = -0.0324x^2 + 0.9286x + 2.9652$	99
50:50-10%	$y = -0.0365x^2 + 0.8826x + 3.1885$	0.99
50:50-15%	$y = -0.0125x^2 + 0.7807x + 3.29$	0.99
50:50-20%	$y = -0.008x^2 + 0.6007x + 3.7692$	0.99
50:50-25%	$y = 0.0018x^2 + 0.5024x + 3.7556$	0.99

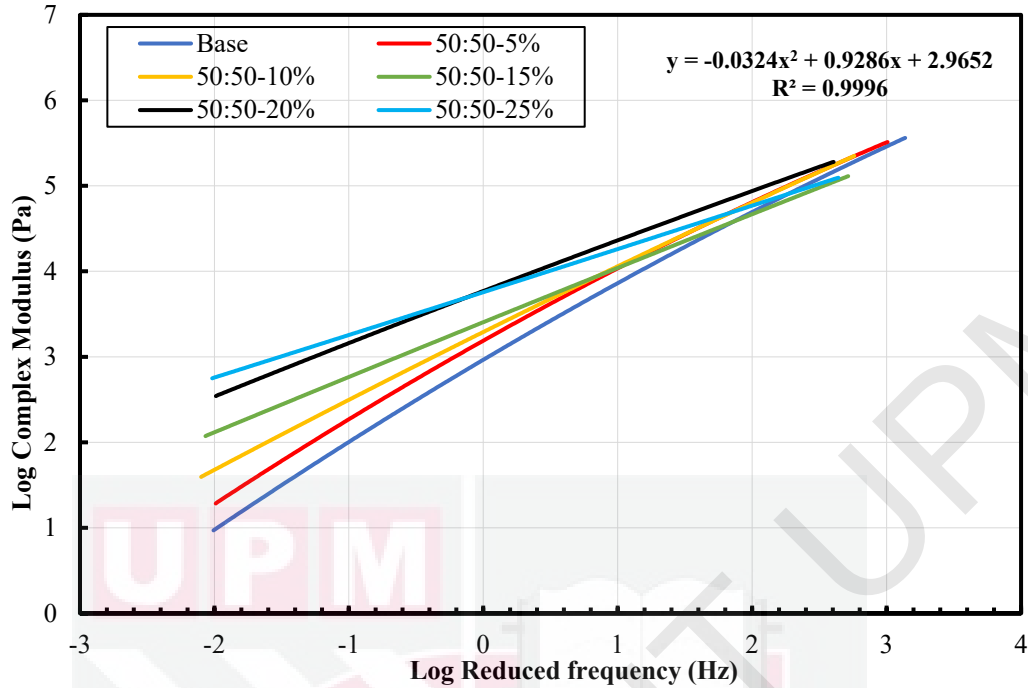


Figure 4.31: Complex modulus master curves of unaged MWCOGa-50:50 at a reference temperature of 65 °C

On the other hand, the G^* of each modified bitumen amalgamates at high frequency or low temperature. The flattening of the G^* curve, which is supported by analogous results at a high rate of load, implies a lower temperature susceptibility. Meanwhile, it is interesting to note that the master curve of 45:55-15% stands out as a less temperature-susceptible curve compared to other modified bitumen. At a lower frequency, it has higher stiffness than 45:55-5%, 45:55-10%, and 45:55-20%, although it becomes less stiff at a higher frequency. This behaviour reveals that the optimal content of 45:55 makes the SBS have the best degree of swelling, which eventually enhances the modified bitumen's elasticity and improves the performance against rutting and fatigue failure. Similar findings were observed in isochronal plots since the incorporation of MWCOG can notably improve the elastic behaviour of MWCOG-modified bitumens at lower and higher temperatures.

Table 4.33: Sigmoidal models-WLF equation parameters and coefficients for RTFO aged bitumens

Blend type	Sigmoidal models-WLF equation parameters					
	δ	α	β	γ	C1	C2
Base	-2.53	9.97	0.20	0.38	9.87	176.18
45:55-5%	-0.17	6.8	-0.008	0.53	14.48	293.08
45:55-10%	-3.73	12.25	-0.32	0.27	20.32	299.12
45:55-15%	2.11	2.98	0.2	1.06	21.11	107.17
45:55-20%	-5.26	17.16	0.001	0.13	6.07	126.04
45:55-25%	2.29	3.78	0.84	0.63	18.19	165.83
50:50-5%	-2.41	9.71	-0.3	0.38	11.43	210.98
50:50-10%	-1.13	8.58	-0.06	0.37	16.48	300.15
50:50-15%	0.05	6.92	0.06	0.37	14.82	277.75
50:50-20%	0.92	5.68	0.001	0.43	33.5	230.14
50:50-25%	1.19	5.54	0.15	0.37	8.97	176.4

Furthermore, the master curves of RTFO aged MWCOG modified bitumens are illustrated in Figure 4.32 and Figure 4.33. The behaviour and trends of the master curves after short-term ageing are similar to the unaged modified bitumen. The variation is mainly caused by the overall increase in the complex modulus of the bitumens. Also, the higher stiffness of RTFO aged MWCOG modified bitumen demonstrated an overlap in the higher temperature zone and lower frequency. The overlap corresponds to the higher stiffness of the modified bitumen. The results of the MWCOG-45:55 and MWCOG-50:50 are further validated by evaluating the sigmoidal model parameters. The δ parameter for both types of the modified bitumen is negative which mainly represents the lower complex modulus at high temperature or on low frequency (Table 4.33). However, MWCOG-50:50 have a significantly high complex modulus compared to the base bitumen which is due to the higher content of the SBS within the bitumen matrix. Whereas on the lower temperature or higher frequencies, the behaviour of the MWCOG-50:50 is more promising due to the sudden shifting of curves downward which represents the bitumen's higher resistance towards the fatigue.

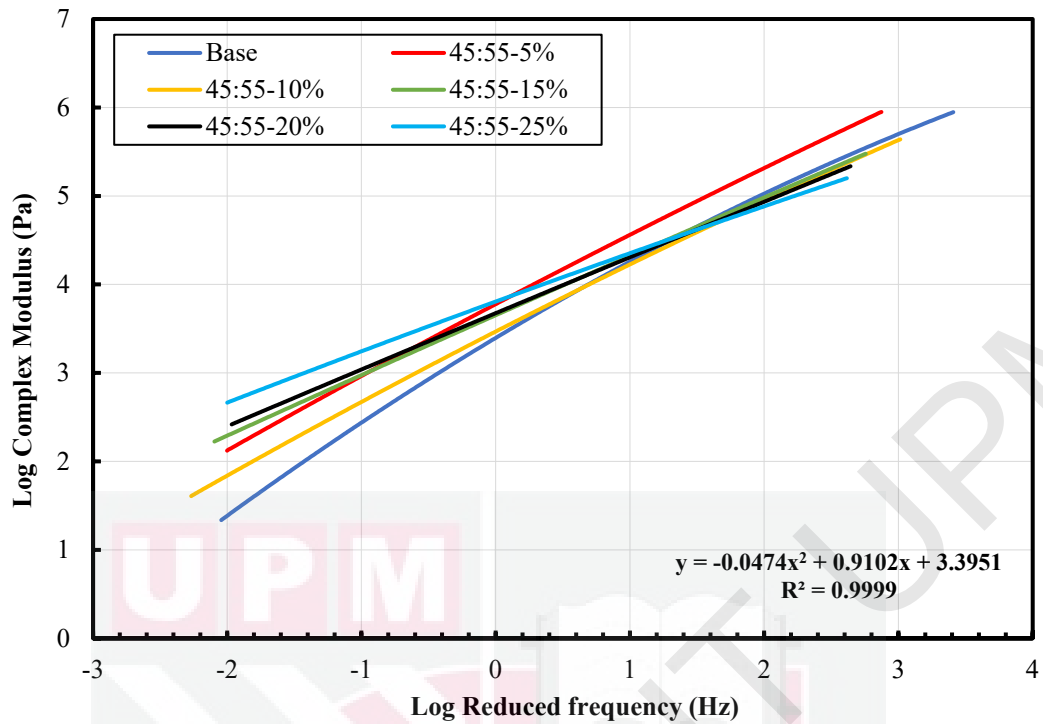


Figure 4.32: Complex modulus master curves of aged MWCOGa-45:55 at a reference temperature of 65 °C

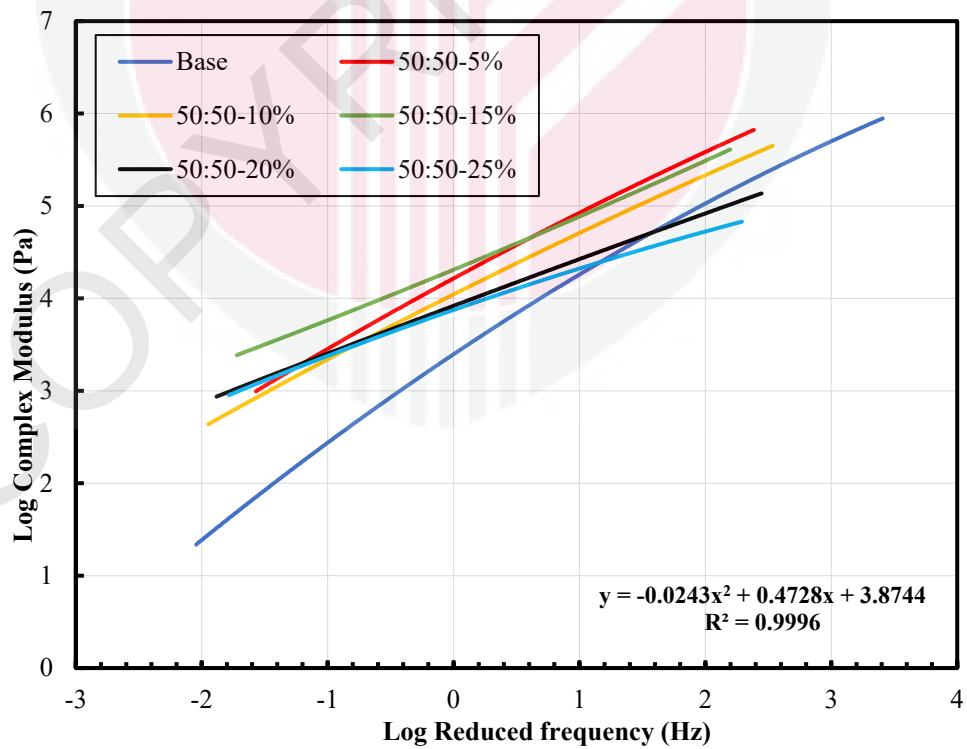


Figure 4.33: Complex modulus master curves of unaged MWCOGa-50:50 at a reference temperature of 65 °C

Table 4.34: Predicting equation of RTFO aged MWCOG modified bitumens

Blend type	Prediction equation	R ²
Base	$y = -0.0474x^2 + 0.9102x + 3.3951$	0.9999
45:55-5%	$y = -0.0144x^2 + 0.7978x + 3.7771$	0.9995
45:55-10%	$y = -0.0186x^2 + 0.7771x + 3.4675$	1
45:55-15%	$y = -0.0038x^2 + 0.6731x + 3.6519$	0.9999
45:55-20%	$y = -0.0023x^2 + 0.6343x + 3.6749$	1
45:55-25%	$y = -0.0082x^2 + 0.5545x + 3.8065$	0.9999
50:50-5%	$y = -0.0261x^2 + 0.7362x + 4.2154$	1
50:50-10%	$y = -0.0192x^2 + 0.6835x + 4.0426$	1
50:50-15%	$y = 0.0143x^2 + 0.5609x + 4.3095$	1
50:50-20%	$y = -0.0055x^2 + 0.5109x + 3.9191$	0.9997
50:50-25%	$y = -0.0243x^2 + 0.4728x + 3.8744$	9996

4.5.5.4 Cole-Cole diagram

The bitumen's viscoelastic properties are highly influenced by energy storage (elastic modulus) and energy loss (viscous modulus) and are typically evaluated using the Cole-Cole diagram. It is a representation of the viscous and elastic zone of the complex modulus. Figure 4.34 to Figure 4.39 display the behaviour of unaged and RTFO aged MWCOG-45:55 and MWCOG-50:50 modified bitumens in terms of viscous (G'') and elastic (G'). Figure 4.34 shows a notable change in G'' and G' at higher temperatures of modified bitumens. The curves of modified bitumen have shifted to the G' portion indicating an improvement in the bitumen elastic behaviour. Nevertheless, a significant portion of BB, 45:55-5% at lower stiffness shows the larger G'' .

Moreover, 45:55-5% has shown higher energy loss than base bitumen at G'' indicating the modified bitumen decline in the ability to store energy. The 45:55-10% and 45:55-15% have shifted significantly towards the elastic axis compared to base bitumen (Figure 4.34). This improvement is likely due to the pre-swelling of SBS in waste cooking oil which promotes the swelling and cross-linking between MWCOG and base bitumen. However, 45:55-20% and 45:55-25% have shown very compacted

curves towards energy storage at higher and lower temperatures, indicating extreme elastic behaviour of modified bitumens due to the excessive content of MWCOG. Conversely, the RTFO aged MWCOG-45:55 modified bitumen results are depicted in Figure 4.35. The performance of short-term aged modified bitumen and base bitumen has further shifted towards the elastic portion. The higher stiffness of the modified bitumen due to the oxidative short-term ageing causes the shift of all modified bitumen.

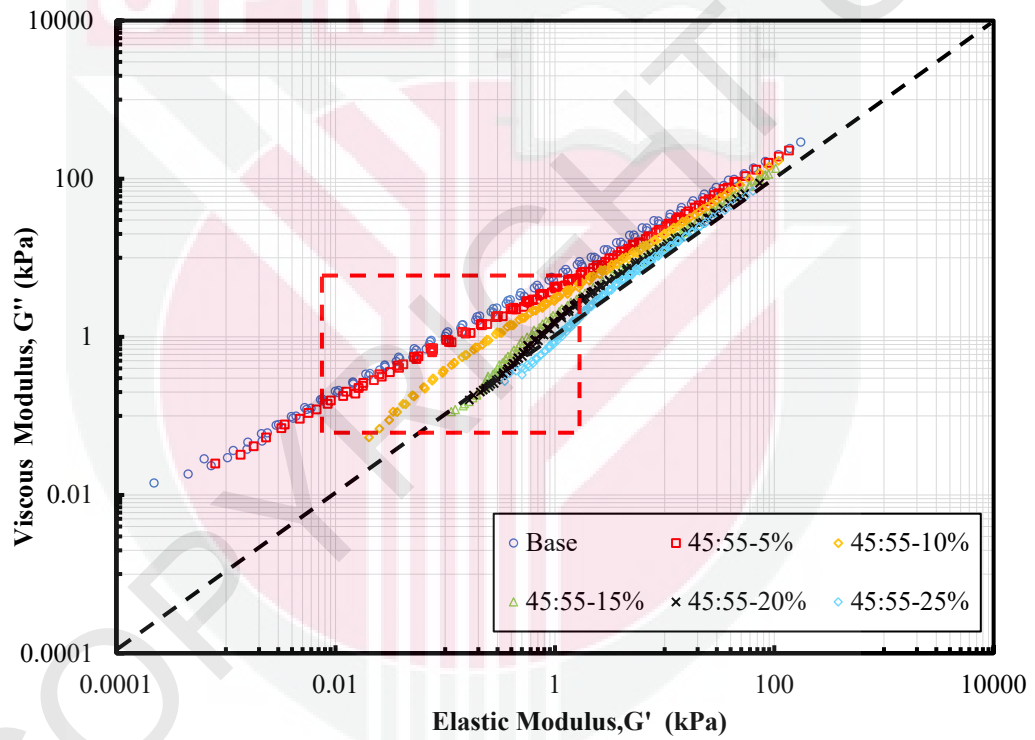


Figure 4.34: Cole-Cole plot of unaged 45:55

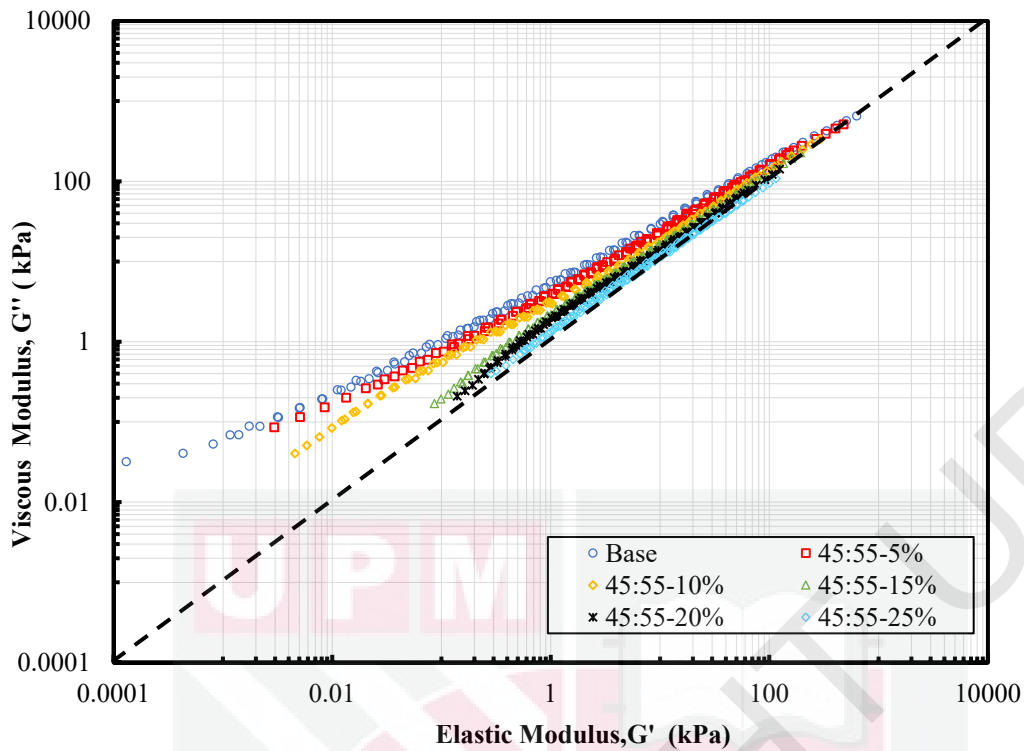


Figure 4.35: Cole-Cole plot of RTFO aged 45:55

Furthermore, the viscoelastic behaviour of the bitumen is mainly evaluated from the angle between the G' and G'' while the line representing the 45° is the indicator. The detailed results of each modified bitumen angle are provided in Table 4.35. It can be observed that the increasing content of the MWCOG has significantly caused the reduction in angle. The trend shifting towards a 45° angle indicates greater viscoelasticity of the bitumen, while the opposite trend suggests otherwise (Figure 4.36 and Figure 4.37). As expected, the rate of increase % of the unaged and RTFO aged bitumen is decreasing on increasing the content of MWCOG. The findings suggest that the modification of base bitumen significantly improves the viscoelastic performance of the modified bitumen.

Table 4.35: Angle between G' and G'' of 45:55 and 50:50 modified bitumens

Blend type	Angle between viscous and elastic modulus (degree)		Rate of decrease (%)	
	Unaged	RTFO aged	Unaged	RTFO aged
Base	61.40	55.88	-	-
45:55-5%	60.86	50.18	-0.88	-10.20
45:55-10%	58.32	51.13	-5.02	-8.50
45:55-15%	53.59	51.35	-12.72	-8.11
45:55-20%	50.71	49.45	-17.41	-11.51
45:55-25%	48.62	43.97	-20.81	-21.31
50:50-5%	59.45	50.99	-3.18	-8.75
50:50-10%	57.60	49.64	-6.19	-11.17
50:50-15%	52.19	46.95	-15.00	-15.98
50:50-20%	48.63	44.35	-20.80	-20.63
50:50-25%	45.64	39.93	-25.67	-28.54

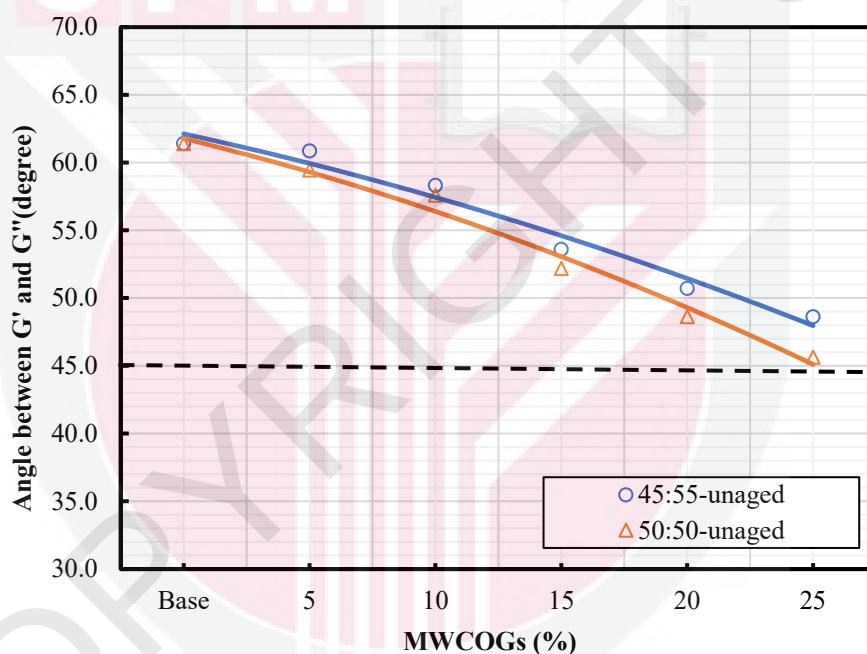


Figure 4.36: Angle between G' and G'' of 45:55 and 50:50 unaged modified bitumens

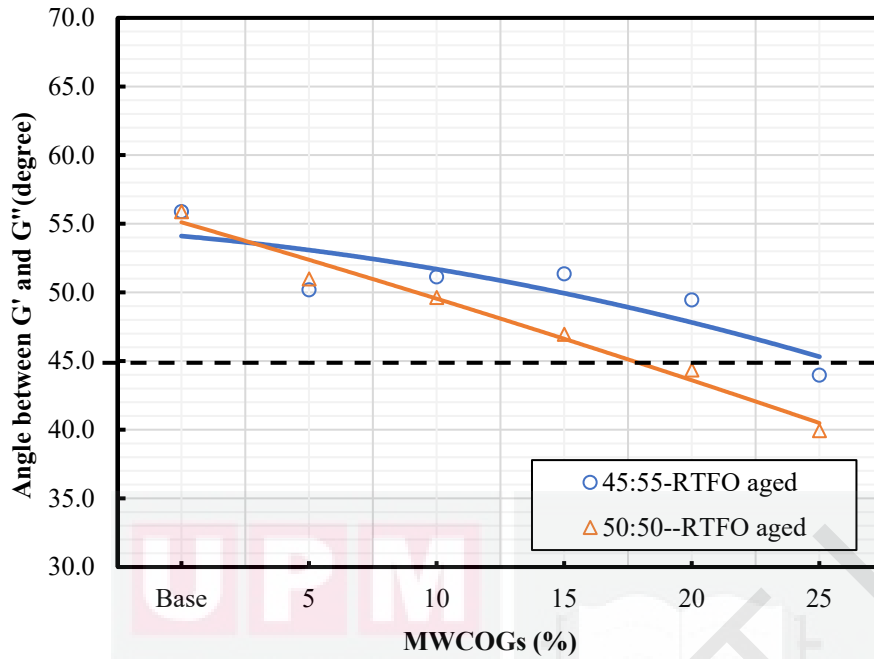


Figure 4.37: Angle between G' and G'' of 45:55 and 50:50 RTFO aged modified bitumens

On the other hand, the MWCOG-50:50 demonstrated a likewise behaviour as MWOCGs-50:50 as shown in Figure 4.38 and Figure 4.39. The findings agree with the results of the earlier discussed Black space diagram and the master curves. The curve shifting of the MWCOG-50:50 is more significant with lower angles compared to the MWCOG-45:55. Figure 4.36 and Table 4.35 provide the reduction of the angle between G' and G'' . The angle of the 50:50-20% is 48° while the 45:55-20% demonstrated an angle of 51° . Moreover, the stiffness of the modified bitumen is further increased after the short-term ageing as expected due to the oxidation of the bitumens (Figure 4.39). Thus, the Cole-Cole diagram is one of the most efficient methods for determining MWCOG and base bitumen compatibility within a bitumen matrix.

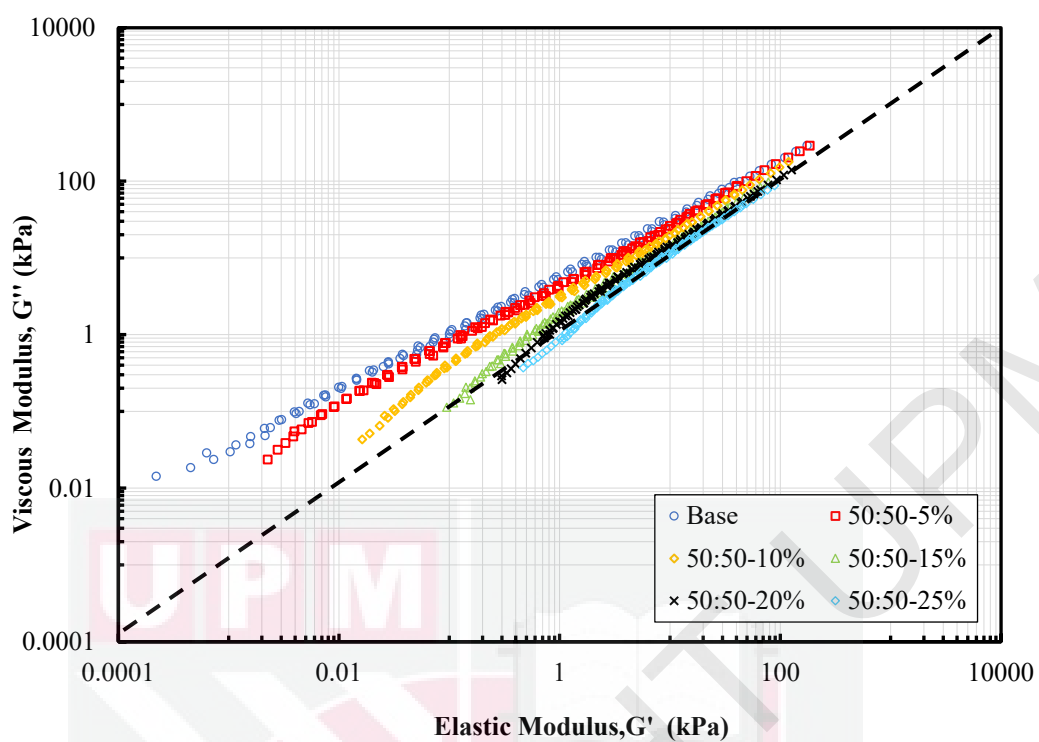


Figure 4.38: Cole-Cole plot of unaged 50:50

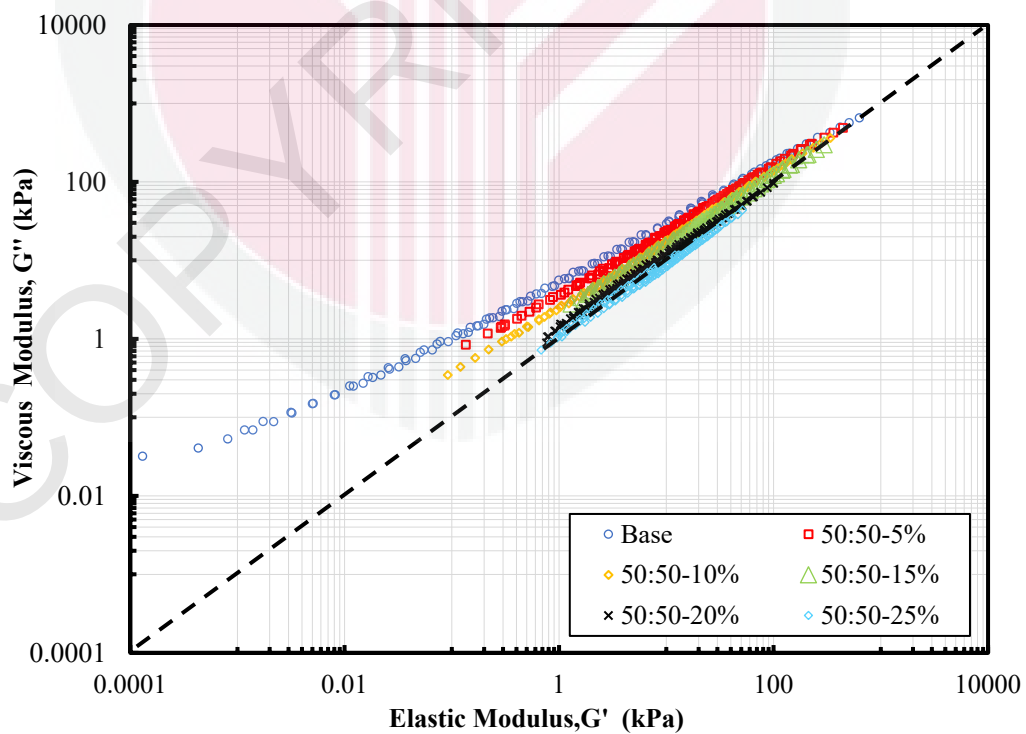


Figure 4.39: Cole-Cole plot of RTFO aged 50:50

4.6 Storage stability test of modified bitumen

The high-temperature storage stability and the separation of properties of the modified is a major concern apart from the bitumen's physical and rheological properties. The polymers and the bitumen blending significantly affect the behaviour of the modified bitumen at higher temperatures (Memon et al., 2021). Moreover, the source of the bitumen and variation in the chemical composition may also influence the storage stability of the modified bitumen at higher temperatures. Separation indices (SIs) based on the G^* at 64 °C temperature were used to characterise the storage stability of the modified bitumens MWCOG-45:55 and MWCOG-50:50. SIs and the complex modulus of the top and bottom parts of the tubes are depicted in Figure 4.40 and Figure 4.41 and tabulated in Table 4.36. The difference in the SIs significantly impacts the modifier network and the elastic behaviour of modified bitumens.

Table 4.36: Complex modulus at 64 °C of MWCOG-45:55 and MWCOG-50:50 modified bitumens after storage stability test

Blend type	Complex Modulus (Pa)			Separation Index (SI)
	Original G^*	Top G^*	Bottom G^*	G^* top/ G^* bottom
Base	1410	1493	1489	1.00
45:55-5%	1530	1711	1705	1.00
45:55-10%	2200	2725	2529	1.08
45:55-15%	2130	2913	2468	1.18
45:55-20%	2620	3624	2984	1.21
45:55-25%	3530	4886	3836	1.27
50:50-5%	1670	1923	1896	1.01
50:50-10%	3560	4298	3915	1.10
50:50-15%	4810	5627	4729	1.19
50:50-20%	5020	6625	5225	1.27
50:50-25%	4980	6936	5100	1.36

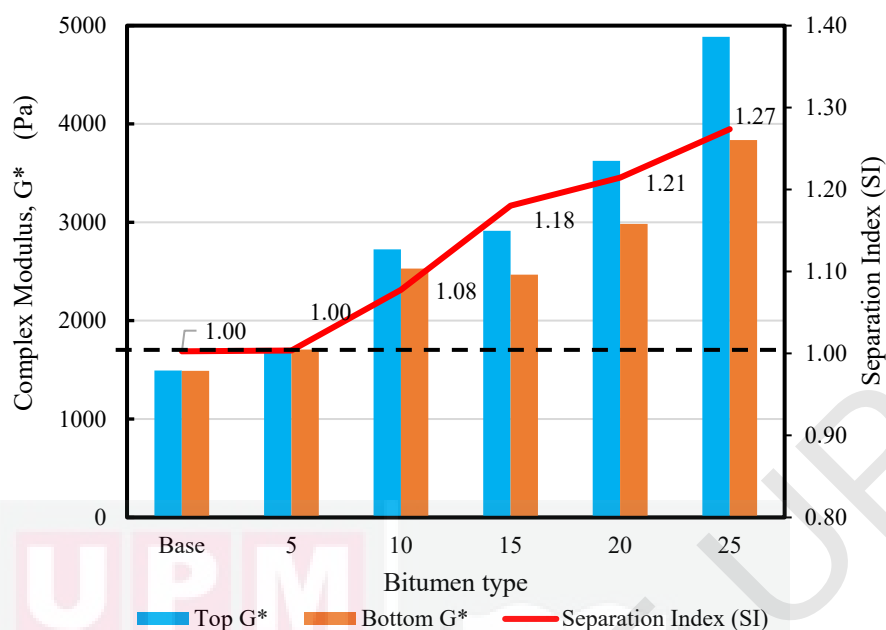


Figure 4.40: Storage stability results of MWCOG-45:55

It is elucidated from the results that the separation indices of the 45:55-5%, 45:55-10%, and 45:55-15%, are nearer to the value of 1.0 indicating the stable modified bitumens. However, on the increasing content of the MWCOG, the indices have increased to 1.30 and 1.34 for the 45:55-20%, and 45:55-25%, respectively. Figure 4.41 exhibited the MWCOG-50:50 modified bitumen with a similar increasing trend of separation indices with enhanced G^* of the top compared to the bottom part. It is revealed from the results that with the lower content (5–15%) of MWCOG-45:55 and MWCOG-50:50, the difference is the top and the bottom G^* are marginal, and indices are nearer to 1.0. It is evident in Figure 4.40 and Figure 4.41 that the MWCOG-45:55 and MWCOG-50:50 modified bitumen (5–15%) are stable in terms of storage stability. The comparative assessment of 45:55 and 50:50 demonstrates that the MWCOG-45:55 have promising indices due to the lower content of the SBS within the bitumen matrix as shown in Figure 4.42. The improvement is due to the dissolution of WCO that promotes the SBS's swelling and homogenous distribution and thus strengthens the

cross-linked network of SBS polymers within the bitumen matrix (Dong et al., 2019).

In contrast, a higher content of MWCOG causes the soft layer on the top of the bitumen and increases the SIs.

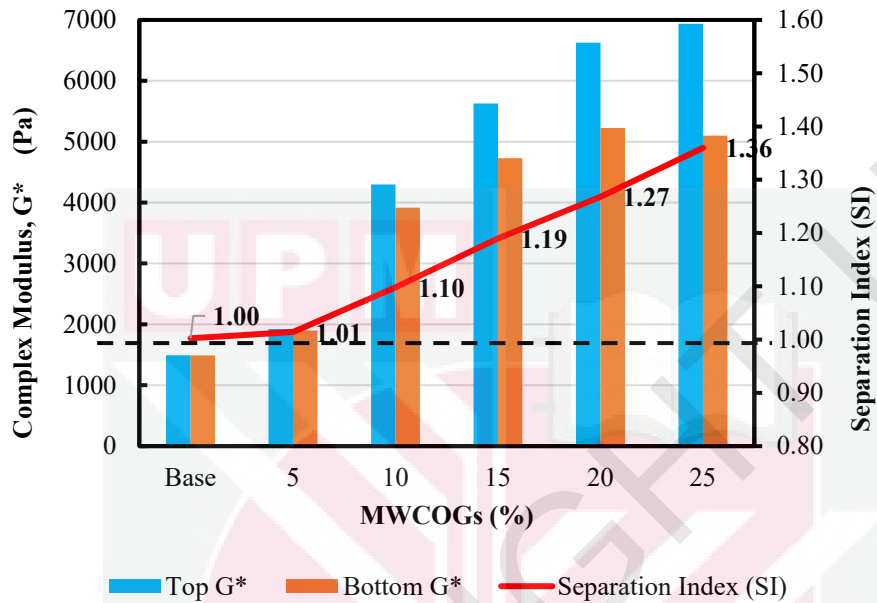


Figure 4.41: Storage stability results of MWCOG-50:50

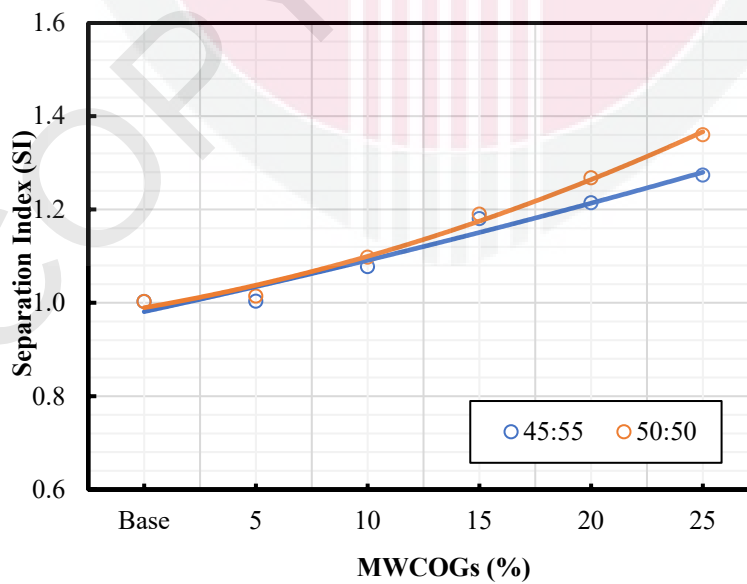


Figure 4.42: Comparative assessment of 45:55 and 50:50 modified bitumen separation indices

4.7 Morphological analysis of MWCOG and modified bitumen

The microscale morphologies of modified waste cooking oil granulates and modified bitumen were examined by using FESEM. Figure 4.43 depicts the morphology and surface texture of the MWCOG-45:55 and MWCOG-50:50 at magnifications of 1 mm and 100 μm . It can be interpreted that the modification of the waste cooking oil with SBS has produced a rubbery solid material with clear physical homogeneity and non-presence of the SBS. The homogeneity of SBS and WCO is mainly caused due to the swelling of the SBS particles by absorbance of the WCO. Conversely, the FESEM micro images of MWCOG-45:55 and MWCOG-50:50 have illustrated the appearance of the SBS particles with different sizes and shape structures. Figure 4.43 depicts the images of the MWCOG-45:55 and MWCOG-50:50 and it can be clearly noticed that the appearance of the SBS particles on MWCOG-45:55 is comparatively less than the MWCOG-50:50. As expected, the higher content of the WCO in the modification process has significantly dissolved the SBS particles with minimum peculiarities. However, Figure 4.43a has demonstrated the few agglomerates which may be caused due to the excessive WCO absorbance by SBS particles. In contrast, the MWCOG-50:50 has more non-homogeneity and appearance of the SBS particles due to the equivalent ratio of the WCO and SBS. Furthermore, the size and structure of the SBS have significantly changed after the modification process with WCO as shown in the FESEM images (Figure 4.43). The average particle sizes of SBS used during the process of modification compared with the size in the SEM images conclude the significant reduction in the size of SBS. Similarly, the fractured surface of the SBS within the MWCOG inferred that it creates better adhesion with the bitumen.

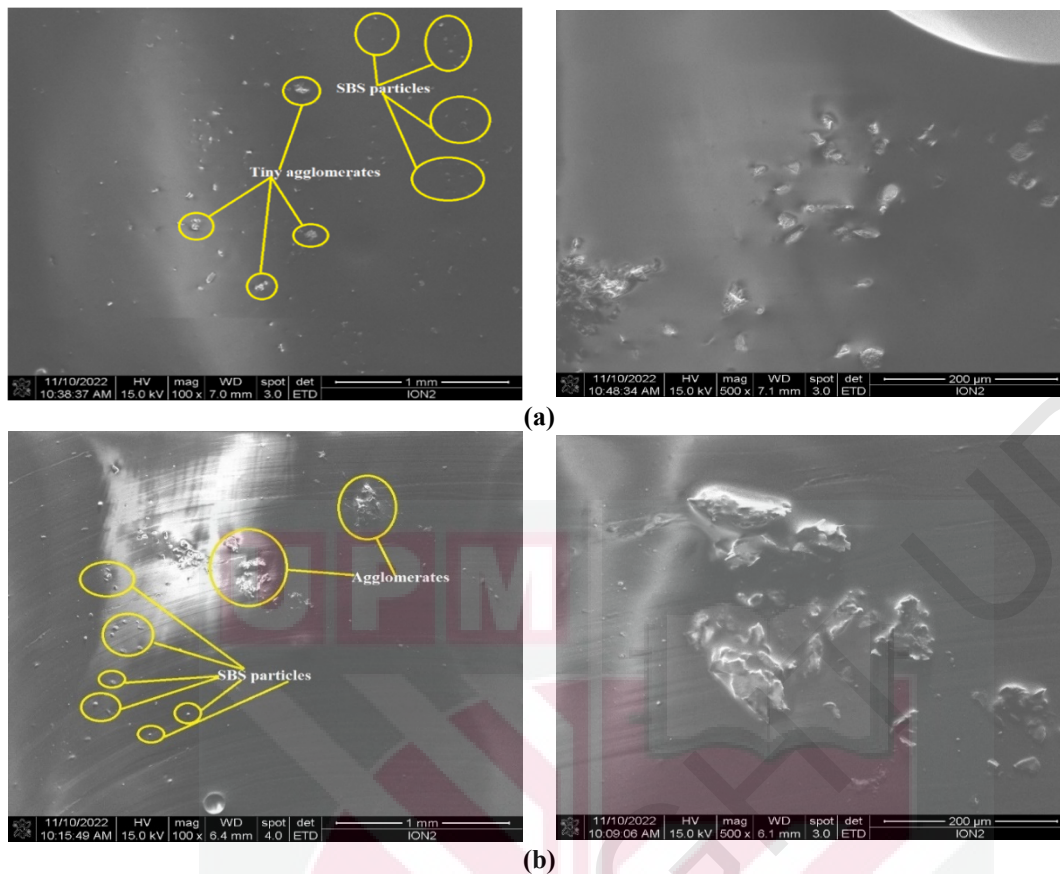


Figure 4.43: SEM images of MWCOG (a) 45:55 (b) 50:50

Figure 4.44 illustrates the compatibility of the MWCOG-45:55 and MWCOG-50:50 with the bitumen. The modified blends 45-55-10% and 50:50-10% were selected to be exploited as standard from both the ratios MWCOG-45:55 and MWCOG-50:50 to identify any changes in the microstructure of modified blends. It was observed that there is no such difference between 45-55-10% and 50:50-10% which further clarifies the principle of the rapid dissolvment of SBS particles in WCO. However, the observed SBS particles in the MWCOG-45:55 and MWCOG-50:50 have fully dissolved within the bitumen matrix as shown in the FESEM images (Figure 4.44). The minor change in the SIs results of the storage stability test further supports the homogeneity and dispersion of the MWCOG within the bitumen. The findings of the FESEM correspond to the improvement in the modified bitumens performance and the homogeneity.

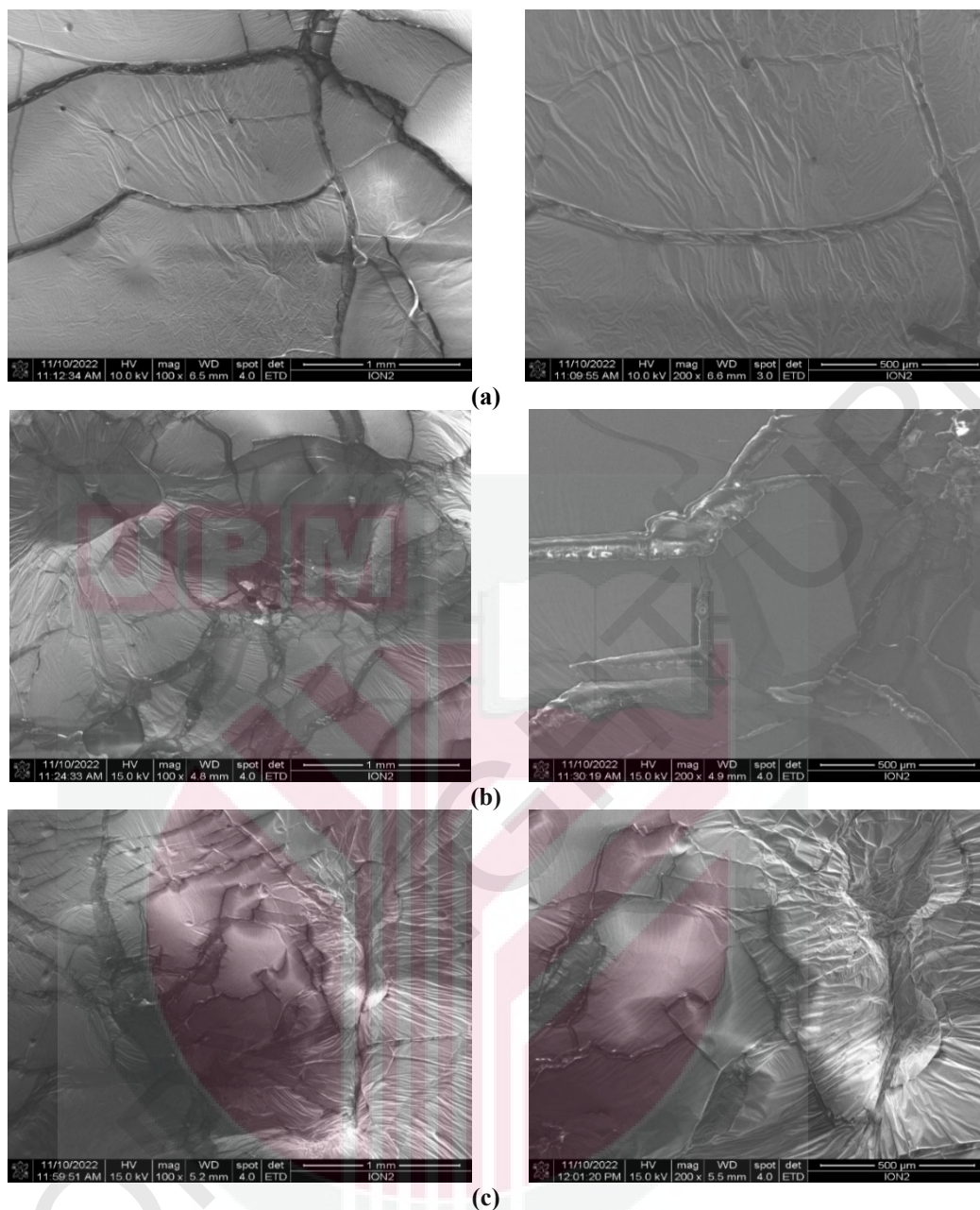


Figure 4.44: FESEM images of base and MWCOG modified bitumen: (a) Base bitumen, (b) 45-55-10%, (c) 50:50-10%

4.8 Energy-dispersive X-ray (EDX) and mapping of modified bitumens

The energy-dispersive X-ray (EDX) analysis was conducted in conjunction with the mapping technique to further clarify the elemental composition of the MWCOG modified bitumens. The EDX analysis is useful for the identification of the elemental

composition while the mapping further enhances the conception of the microscale distribution. Figure 4.45 and Figure 4.46 present the EDX and mapping results to elaborate the elemental composition of the MWCOG-45-55 and MWCOG-50:50 modified bitumen respectively. The modified blends 45-55-10% and 50:50-10% were selected to be exploited as standard from both the ratios MWCOG-45:55 and MWCOG-50:50 to identify any changes in the chemical composition. The EDX analysis and mapping assessment of the MWCOG modified bitumens discerns a notable concentration of carbon. The observed increased carbon content in the composite structure of SBS and WCO is attributed to their inherent hydrocarbon structures. This inherent composition significantly contributes to the higher carbon content, aligning with the polymer characteristics of SBS. Additionally, the organic nature of WCO imparts a noteworthy increase in the overall carbon content within the MWCOG. Moreover, the bitumen composition further increases the carbon content as 80-90% of the bitumen is carbon. These findings provide valuable insights into the elemental composition of MWCOG, important for understanding their structural properties.

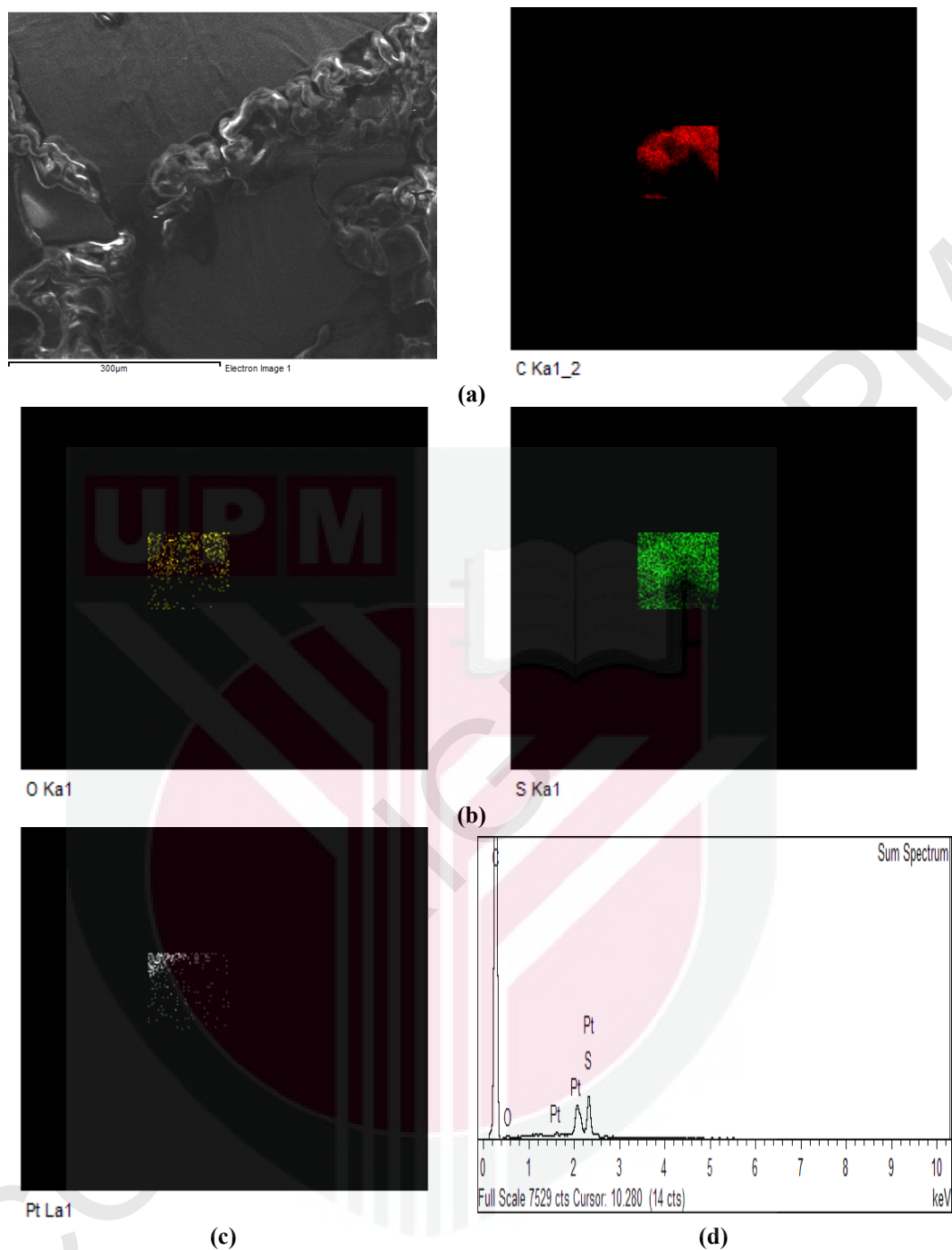


Figure 4.45: FESEM mapping images and EDX spectra of modified bitumen 45:55 (a),(b),(c) Mapping images (d) EDX spectra.

Table 4.37: Elemental composition of 45:55 modified bitumen

Element	Weight (%)	Atomic (%)	Energy level
Carbon (C)	87.13	96.86	K shell
Oxygen (O)	1.09	0.91	K shell
Sulphur (S)	4.10	0.12	K shell
Platinum (Pt)	7.65	0.52	M shell
Total	100		

Furthermore, the mapping results highlight the spatial distribution of carbon within the composite, aligning with the polymeric structure of SBS the organic composition of WCO and the higher concentration in the composition of the bitumen. This emphasizes the successful amalgamation of all constituents in the composite material. Table 4.37 and Table 4.38 provide the chemical composition and the percentage of all elements identified within the bitumen matrix. The observed carbon higher concentration in the composite material and with bitumen holds a noteworthy implication for the materials in terms of durability, thermal stability and mechanical strength. The mapping of the MWCOG modified bitumen further revealed the homogeneous blending of the MWCOG within the bitumen which is an important factor contributing to the materials' desired properties.

Conversely, the oxygen lower content in composite material may be attributed to the inherent composition of the MWCOG and the bitumen. The Edx analysis has further highlighted the presence of sulphur in MWCOG-45:55 and MWCOG-50:50 modified bitumen. The bitumen mainly contains traces of sulphur as it is the by-product of the crude oil which naturally contains 1- 4%. The carbon abundance nature of the SBS and the dominance of the triglycerides which are rich in carbon in WCO contribute slightly to the oxygen signal. This observation is further validated by mapping, which shows a spatial distribution aligning with the expected composition. The minor variation in the carbon and oxygen content in the MWCOG-45:55 and MWCOG-50:50 can be attributed to the minimal variation in the ratio of SBS and WCO and the sulphur content elucidates the similar concentration. The presence of platinum in the results is not indicative of the material's inherent chemical composition. Instead, it arises from the coating applied to enhance conductivity for more effective analysis purposes.

Table 4.38: Elemental composition of 50:50 modified bitumen

Element	Weight (%)	Atomic (%)	Energy level
Carbon (C)	58.23	93.04	K shell
Oxygen (O)	1.23	1.47	K shell
Sulphur (S)	2.99	1.79	K shell
Platinum (Pt)	37.55	3.69	M shell
Total	100		

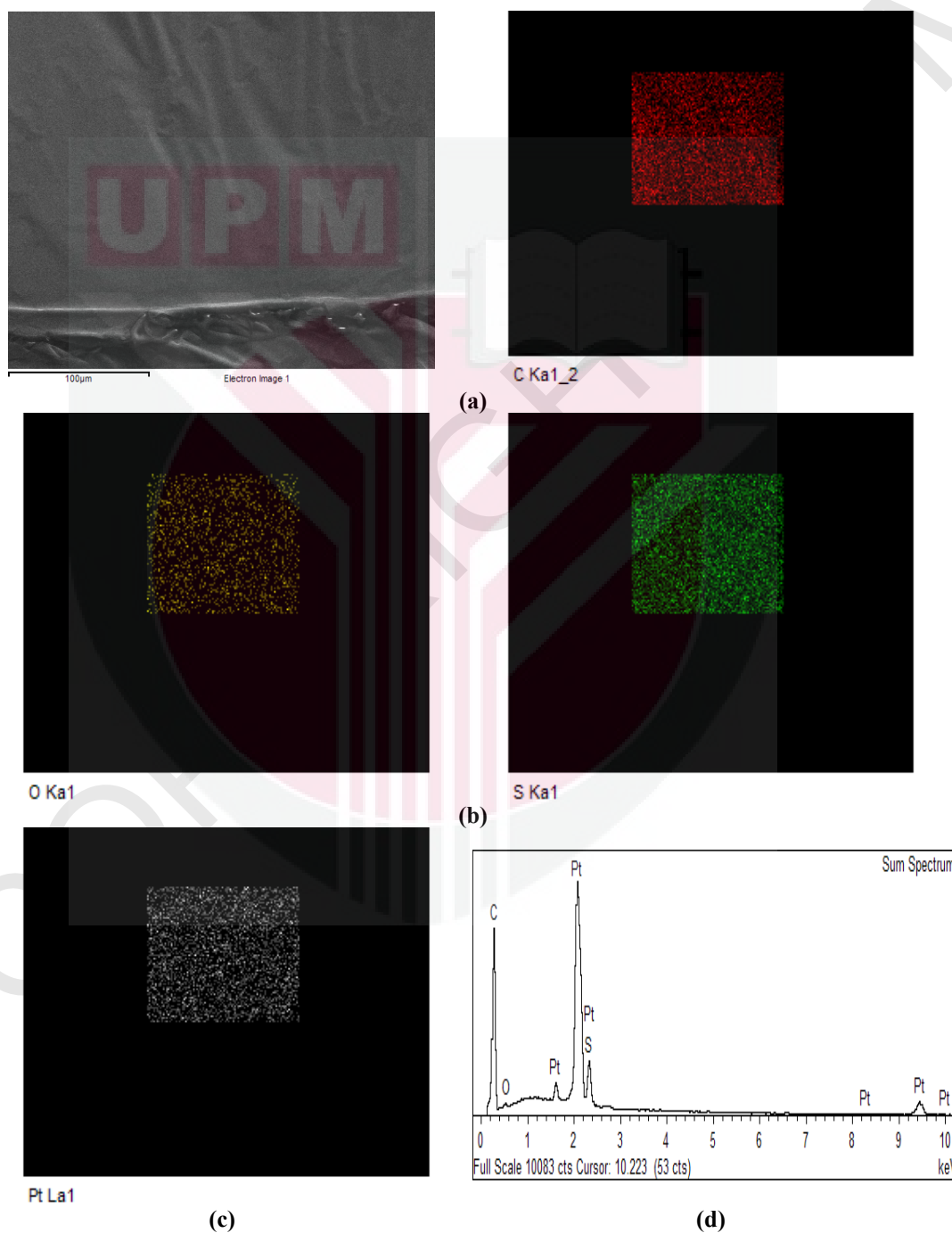


Figure 4.46: FESEM mapping images and EDX spectra of modified bitumen 50:50 (a),(b),(c) Mapping images (d) EDX spectra

4.9 FTIR analysis of selected blends

Figure 4.47 shows the BB and modified bitumens FTIR spectra. It is shown that there are no peaks $>3000\text{ cm}^{-1}$ that belong to the O–H groups. Hence, proving that no water was present in any sample. The similarity in the FTIR spectra peaks of WCO and BB can be observed, indicating that both have functionally similar grouping. The two major peaks for BB at 2856 cm^{-1} and 2922 cm^{-1} are attributed to C–H stretching from aliphatic chains (Saowapark et al., 2019). Alternately, the peaks at 1374 cm^{-1} and 1458 cm^{-1} are attributed to the C–CH₃ methylene asymmetry. Additionally, the weak peaks at 730 cm^{-1} are connected to C–H vibrations in the benzene ring (Zhang and Hu, 2016). Moreover, WCO had few functional groups the high absorption peaks at 1257 cm^{-1} , 1743 cm^{-1} , and 721 cm^{-1} , associated with C=O stretching and indicating acids and esters (Liu et al., 2020; Niu et al., 2021b).

Additionally, the FTIR spectrum of the SBS exhibits peaks at 967 cm^{-1} (which defines the butadiene block) as well as at 3060 cm^{-1} and 700 cm^{-1} (characterising the styrene block) (Liu et al., 2020). However, MWCOG-45:55 and MWCOG-50:50 have peaks of esters and ketones at 1743 cm^{-1} , 967 cm^{-1} , and 700 cm^{-1} that identify dominance of WCO, butadiene, and styrene block, respectively. When MWCOG-45:55 and MWCOG-50:50 were added into base bitumen by 10wt%, the 45:55-10% and 50:50-10% spectra show no significant difference in the location of peaks. This identifies that there is no noticeable difference in the functional groups. However, the absorptions of peaks at a range of 1850 cm^{-1} – 1650 cm^{-1} of 10A and 10B are more intense than the peak of BB. A similar peak has been identified in the WCO, MWCOG-45:55, and MWCOG-50:50 spectra which corresponds to the dominance of the ester

and the ketones at 1743cm^{-1} (Lyu et al., 2022). These results are comparable with the earlier stated studies (Azahar et al., 2016c; Liu et al., 2020; Lyu et al., 2022).

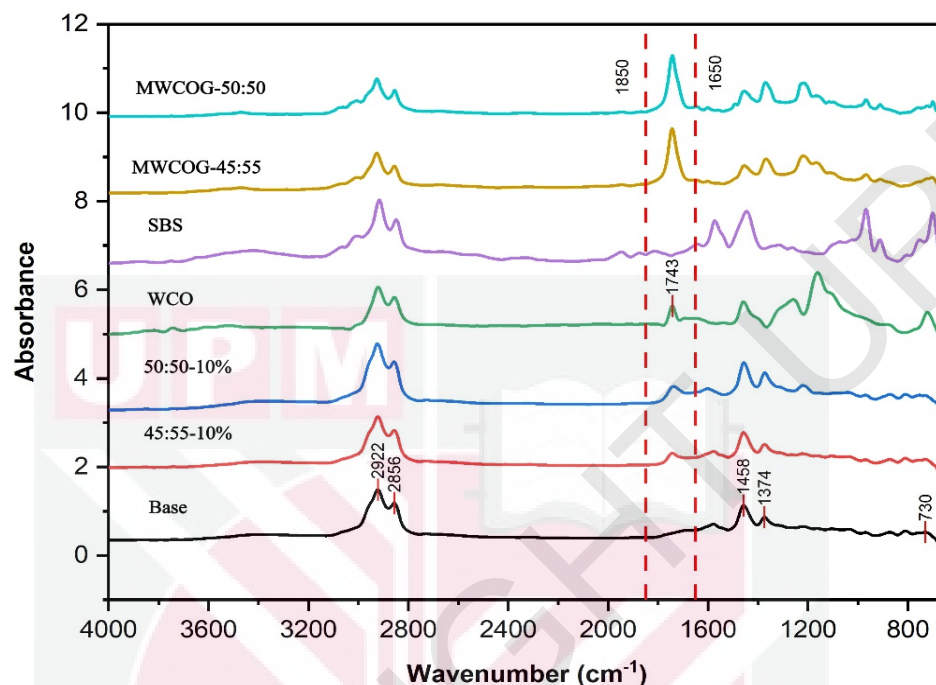


Figure 4.47: FTIR spectra of MWCOG-45:55 and MWCOG-50:50

4.10 Process of elimination for blends

The MWCOG modified bitumen was extensively analysed in the previous section to evaluate the promising modified blends for further characterization. The 11 modified blends i.e., Base bitumen, 45:55-5%, 45:55-10%, 45:55-15%, 45:55-20%, 45:55-25%, 50:50-5%, 50:50-10%, 50:50-15%, 50:50-20% and 50:50-25% were characterized for their rheological, morphological, stability and the chemical composition and modified bitumens with promising performance were opted for the mechanical performance analysis. The analysis suggests that a higher content of MWCOG for ratios 45:55 and 50:50 might not be promising for utilization in bitumen modification. The dynamic

rheological evaluation has shown that the incorporation of the MWCOG of more than 15% has caused inconsistencies in the performance of the bitumen. Moreover, the higher incorporation has shifted the bitumen towards the higher elastic zone which stiffens the bitumen with increased viscosity and is probably not suitable for a long service life of the pavements. Therefore, the incorporation of the higher content of the WCOGs is not feasible for modification of the bitumens. In a nutshell, the modified bitumens 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15% were opted to evaluate their performance in asphalt mixtures.

4.11 Summarised results of Objective 2

Table 4.39 presents the summarised results of the MWCOG-45:55 and MWCOG-50:50 modified bitumens. The results discussed in the previous sections of objective 2 of the study have demonstrated a varied performance on the inclusion of the various concentrations of the modified cooking oil granulates. Based on the viscosity results, the increasing content of the MWCOG has increased the stiffening and improved the temperature susceptibility of the base bitumen. Adding 5–25 wt.% of MWCOG-45:55 improves the viscosities in the range of 513–3512.2 cp at 135 °C. However, the MWCOG-50:50 displayed a slightly higher viscosity in the range of 562.1–2988.2 cp. However, the modified bitumen 45:55-25% and 50:50-25 are undesirable owing to higher viscosities beyond the SHRP specifications. The isochrones of the modified bitumens indicated the enhancement in G^* on increasing the concentration of MWCOG and as expected the δ decreases showing the elastic behaviour of bitumens. It is noteworthy that the performance grading of the base bitumen is improved from 64 °C to 76 °C whilst adding the 10% of MWCOG-50:50. Moreover, the Black space

diagram curves have shifted towards the lower δ with smooth curves indicating the improvement in the performance of the modified bitumens, and 45:55-25% and 50:50-25% curves are not desirable, indicating the marginal change in δ at higher and lower temperatures. The storage stability test explicated that the separation indices (SIs) based on the complex modulus at a temperature of 64 °C of the modified bitumen are within the specified range regardless of the 45:55-25% and 50:50-25%. The modified blends 45:55-10% and 50:50-10% were selected to be exploited as standard to identify any changes in the microstructure of modified blends. It was observed that there is no such difference between 45:55-10% and 50:50-10% which further clarifies the principle of the rapid dissolvment of SBS particles in WCO. In a nutshell, the modified bitumen 45:55-15% and 50:50-10% have shown optimal rheological performance and incorporation of the MWCOC beyond 15% will not be promising for long-term performance. Therefore, the 45:55-20%, 45:55-25%, 50:50-20% and 50:50-25% will be omitted from the Marshall mixture design for the determination of the OBC in objective 3 of the study.

Table 4.39: Summarised results of MWCOG-45:55 and MWCOG-50:50 modified bitumen

Blend type	Viscosity (Pa.s) @ 135 °C	Mixing temperature °C	Fatigue @ 16 °C (kPa)	Rutting @ 64 °C (kPa)	Complex modulus at 14Hz & 65 °C	Failure temperature °C	Performance grading
Base	0.429	160	5950	1.43	9.15	67.8	64
45:55-5%	0.513	163	4210	1.61	15.60	68.2	64
45:55-10%	0.806	173	2900	2.35	15.60	72.9	70
45:55-15%	1.350	181	2022	2.44	8.23	76.0	76
45:55-20%	1.987	191	1490	3.21	10.30	77.1	76
45:55-25%	3.512	>200	1247	5.43	10.80	80.1	76
50:50-5%	0.562	166	4321	1.7	12.80	67.3	64
50:50-10%	0.946	180	3225	3.70	13.30	76.3	76
50:50-15%	1.683	192	2300	5.22	12.40	79.9	76
50:50-20%	2.127	>200	1832	5.78	29.30	82.0	82
50:50-25%	2.988	>200	1525	7.15	23.30	82.0	82

4.12 Hot mix asphalt mix design (Objective 3)

The Marshall Mix design, as outlined in (D1559, 1989) and (ASTM D6926, 2016) was employed to determine the optimum bitumen content (OBC) of asphalt mixtures. The seven modified bitumens including the base bitumen as discussed in section (4.10) were utilized to prepare the Marshall cylindrical specimens. The 105 cylindrical specimens were prepared using the seven selected MWCOG modified bitumens. The specimens were compacted by applying 75 blows using a Marshall compactor on each side of the specimens. Whereas the 35 loose specimens were prepared to be used for the determination of the theoretical maximum density. Three replicates were prepared at each bitumen content ranging from 4.0% to 6.0% to ascertain the Optimum Bitumen Content (OBC). The specimen's volumetric properties were assessed, followed by the Marshall stability and flow test, along with the determination of resilient modulus and OBC using the Asphalt Institute method.

4.12.1 Aggregate gradation

In asphalt mixtures, selecting the right aggregates is important for performance. Typically, these mixtures contain coarse and fine aggregates along with mineral fillers. The sizes of these aggregates are critical for achieving the optimal gradation in the mix. In this study, the AC 14 gradation, as per JKR specifications, was used for the Marshall mix design. The granite aggregate was sieved in accordance with ASTM (2006) standards. Table 4.40 provides the particle size distribution and the aggregate sizes of AC14 for preparing cylindrical specimens. The medium gradation was chosen to identify the most suitable gradation in terms of density, stability, and air voids of

4% (Figure 4.48). The specimen comprises various sizes of aggregates with a total weight of 1150 g following the AC14 to prepare the cylindrical specimens.

Table 4.40: Specification of AC14 HMA aggregate gradation

Sieve size (mm)	Passing (Lower-Upper) (%)	Passing (Medium) (%)	Retained (%)
20	100	100	0
14	90-100	95	5
10	76-86	81	14
5	50-62	56	25
3.35	40-54	47	9
1.18	18-34	26	21
0.425	12-24	18	8
0.15	6-14	10	8
0.075	4-8	6	4
Pan	Filler	0	6
Total			100

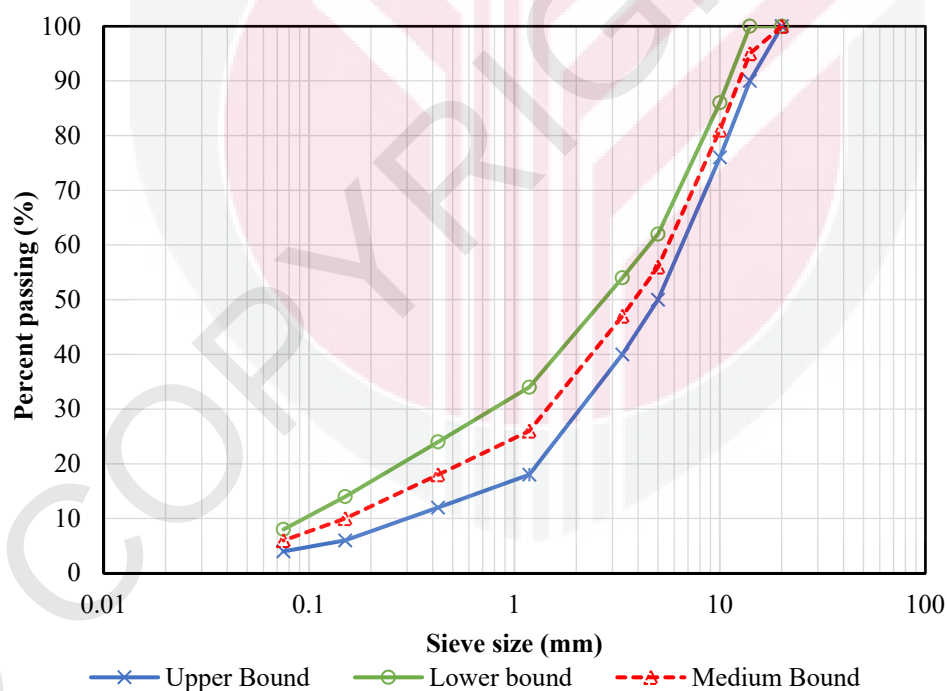


Figure 4.48: Aggregates particle size distribution curves

4.12.2 Marshall mix design and specimen preparation

Following the process of elimination, the seven modified bitumen were selected for asphalt mixture design and evaluation of the OBC. The selected bitumen blends including the base bitumen are 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15%. The 15 cylindrical specimens were prepared for each asphalt mixture design with bitumen content in a range of 4% to 6% with 0.5% fixed interval. The triplicate of cylindrical specimens was compacted at each bitumen content interval. A total of 140 specimens were prepared for the determination of the OBC of which 105 were compacted while the remaining 35 were loose specimens for the TMD. The air voids of 4% were targeted for the selection of the OBC to mainly simulate the field conditions. The mixing and compaction temperatures were opted from the viscosity-temperature relationship for the base and the MWCOC modified blends and discussed in detail in section 4.5.1.

4.12.3 Volumetric properties of all mixtures

The volumetric properties of the cylindrical specimens were determined at each varying bitumen content. The variations in these properties have a significant influence on the asphalt mixtures. The related equation for the determination of the volumetric properties is detailed in section 3.12.3, Chapter 3. The equations (3.5 to 3.9) are used for determining the properties and the calculation for the control mixture at a bitumen content of 4.0% is as below.

- Theoretical maximum density (G_{mm})
- Bulk specific gravity (G_{mb})

- Voids in total mix (VTM)
- Voids in mineral aggregates (VMA)
- Void filled with bitumen (VFB)

$$G_{mm} = \frac{A}{A - (C - B)} = \frac{1194.3}{1194.3 - (2543.1 - 1843.1)} = 2.459$$

$$G_{mb} = \frac{A}{B - C} = \frac{1184.7}{1190.2 - 678.9} = 2.317$$

$$VTM(\%) = \frac{G_{mm} - G_{mb}}{G_{mm}} \times 100 = \frac{2.459 - 2.317}{2.459} \times 100 = 5.77$$

$$VMA \% = 100 \times \left(1 - \frac{G_{mb}(1 - P_b)}{G_{sb}} \right) = 100 \times \left(1 - \frac{2.317(1 - 0.04)}{2.613} \right) = 14.87$$

$$VFB \% = 100 \times \frac{VMA - VTM}{VMA} = 100 \times \frac{14.87 - 5.78}{14.87} = 61.12$$

The control mixture volumetric properties are provided in Table 4.41 and illustrated in Figure 4.49. However, the asphalt mixtures 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15% volumetric properties are provided in **Appendix B**. The properties of the control mixture at OBC are presented in Table 4.42 mentioning the JKR specifications. Whereas all other modified asphalt mixture properties after the determination of the OBC are summarised in Table 4.43. It can be observed that the OBC of asphalt mixtures are reduced with increasing content of the MWCOG (Table 4.43). However, there is an increase in the bulk density of the modified bitumens which corresponds to the improvement of the mixtures. The improvement is further validated with the enhanced resilient modulus of the asphalt mixture compared to the control mixtures. For instance, 45:55-5% demonstrated a

resilient of 4211 Mpa which is higher than the control mixture of 3509 Mpa. Similarly, increased Marshall stability has been observed which ultimately causes the improvement in the mixture with lower OBC. The overall finding of all seven asphalt mixture mixes design volumetric properties satisfied the AC14 JKR specifications and reflects that the mixtures were properly designed.



Table 4.41: Volumetric properties of control mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)			Height correlation ratio	Stability (kN)	Corrected Stability (kN)	Flow (mm)	Resilient Modulus (MPa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFB					
4.0-I	4.0	64.6	1184.7	678.9	1190.2	2.317	2.459	5.78	14.87	61.12	0.97	16.58	16.08	3.44	2871
4.0-II	4.0	64.4	1180.9	667.8	1185.2	2.282	2.459	7.19	16.15	55.49	0.97	12.88	12.49	3.25	3025
4.0-III	4.0	64.4	1184.7	672.7	1181.3	2.329	2.459	5.28	14.42	63.41	0.97	14.89	14.44	3.09	3292
Average		64.4	1183.43	673.133	1185.6	2.310	2.459	6.08	15.15	60.02	0.97	13.89	13.47	3.26	3063
4.5-I	4.5	65.1	1194	682.4	1197.1	2.320	2.441	4.98	15.22	67.25	0.96	15	14.40	5.01	2985
4.5-II	4.5	64.63	1195.7	684.4	1197.3	2.331	2.441	4.51	14.80	69.49	0.97	15.6	15.13	5.83	3601
4.5-III	4.5	63.8	1175.8	671.7	1177.4	2.325	2.441	4.77	15.02	68.27	0.99	15	14.85	3.73	3522
Average		64.5	1188.5	679.5	1190.6	2.325	2.441	4.755	15.01	68.34	0.97	15.20	14.79	4.86	3369
5.0-I	5.0	65.3	1177.3	675.2	1180.9	2.328	2.424	3.96	15.36	74.21	0.95	16.83	15.99	3.49	4210
5.0-II	5.0	64.53	1192.9	687.9	1199.7	2.331	2.424	3.85	15.26	74.78	0.97	15.88	15.40	5.84	4459
5.0-III	5.0	66.6	1191.8	686.4	1197.6	2.331	2.424	3.82	15.24	74.91	0.97	11.21	10.87	4.7	3337
Average		65.5	1187.3	683.2	1192.7	2.330	2.424	3.88	15.29	74.63	0.96	16.36	15.70	4.68	4002
5.5-I	5.5	63.9	1201.4	692.3	1206.8	2.335	2.407	2.99	15.55	80.80	1.0	16.34	16.18	5.38	2362
5.5-II	5.5	64.53	1207.9	695.5	1216.1	2.320	2.407	3.60	16.09	77.61	0.97	16.22	15.73	5.26	2281
5.5-III	5.5	65.53	1208.7	693.4	1213.2	2.325	2.407	3.39	15.90	78.68	1.0	16.13	15.32	5.67	2834
Average		64.7	1206.0	693.7	1212.0	2.327	2.407	3.326	15.85	79.03	0.97	16.23	15.74	5.44	2492
6.0-I	6.0	63.97	1203.6	691.5	1207.7	2.332	2.390	2.44	16.12	84.85	0.98	14.26	13.97	5.18	1780
6.0-II	6.0	64.1	1200.5	694.4	1206.4	2.345	2.390	1.90	15.65	87.89	0.98	12.7	12.45	5.23	2092
6.0-III	6.0	64	1201.5	692.5	1208.9	2.327	2.390	2.65	16.30	83.74	0.98	12.65	12.40	5.5	1741
Average		64.0	1201.9	692.80	1207.7	2.334	2.390	2.329	16.02	85.49	0.98	13.20	12.94	5.30	1871

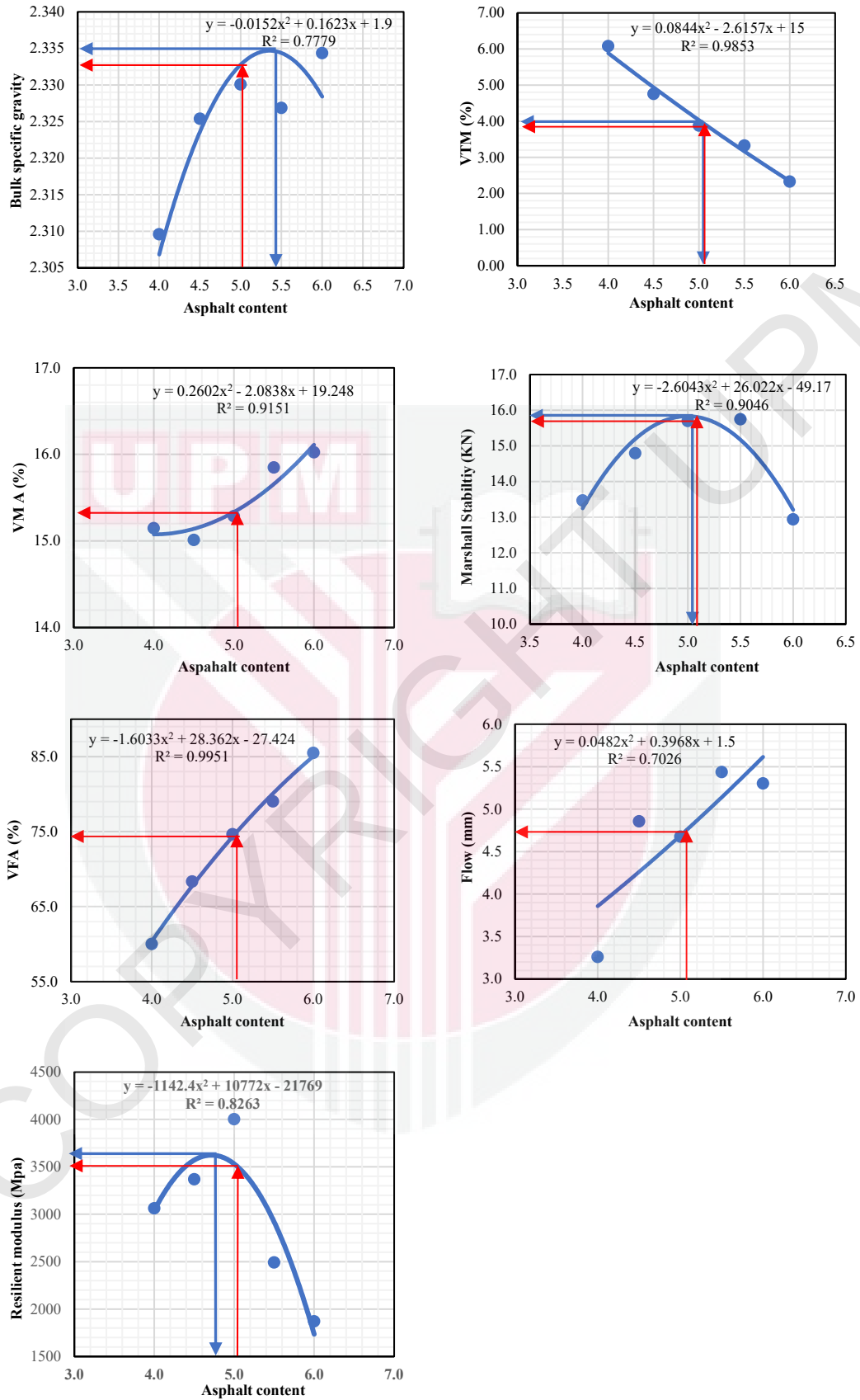


Figure 4.49: Optimum bitumen content determination plots for control mixture

Table 4.42: Marshall mix design results of control mixture

Marshall Properties	Values	Specifications
Optimum bitumen content (%)	5.0375	-
Bulk density	2.31	-
Stability (KN)	15.82	>13KN
VTM (%)	3.97	3-5%
VMA (%)	15.35	>15%
Resilient Modulus (Mpa)	3504.9	>2500
Flow (mm)	4.72	2.0-5.0 (mm)
VFB (%)	74.76	70-80%

Table 4.43: Summarised volumetric properties of seven mixture designs

Mixture type	OBC (%)	Bulk density	Stability (kN)	VTM (%)	VMA (%)	Flow (mm)	VFB (%)	RM (MPa)
Control	5.0375	2.331	15.82	3.965	15.35	4.722	74.76	3504.94
45:55-5%	4.9025	2.333	16.22	4.077	15.31	4.617	73.45	4211.8
45:55-10%	4.9225	2.338	17.83	3.702	15.07	4.284	75.5	3558.9
45:55-15%	4.91	2.349	16.43	3.609	15.03	4.851	76.21	2520.86
50:50-5%	4.8925	2.341	18.05	3.378	15.149	4.341	74.18	4858.75
50:50-10%	4.8875	2.3427	19.01	3.798	15.09	4.74	74.9	3484.27
50:50-15%	4.925	2.3652	17.85	2.402	13.96	4.51	82.93	3165.78

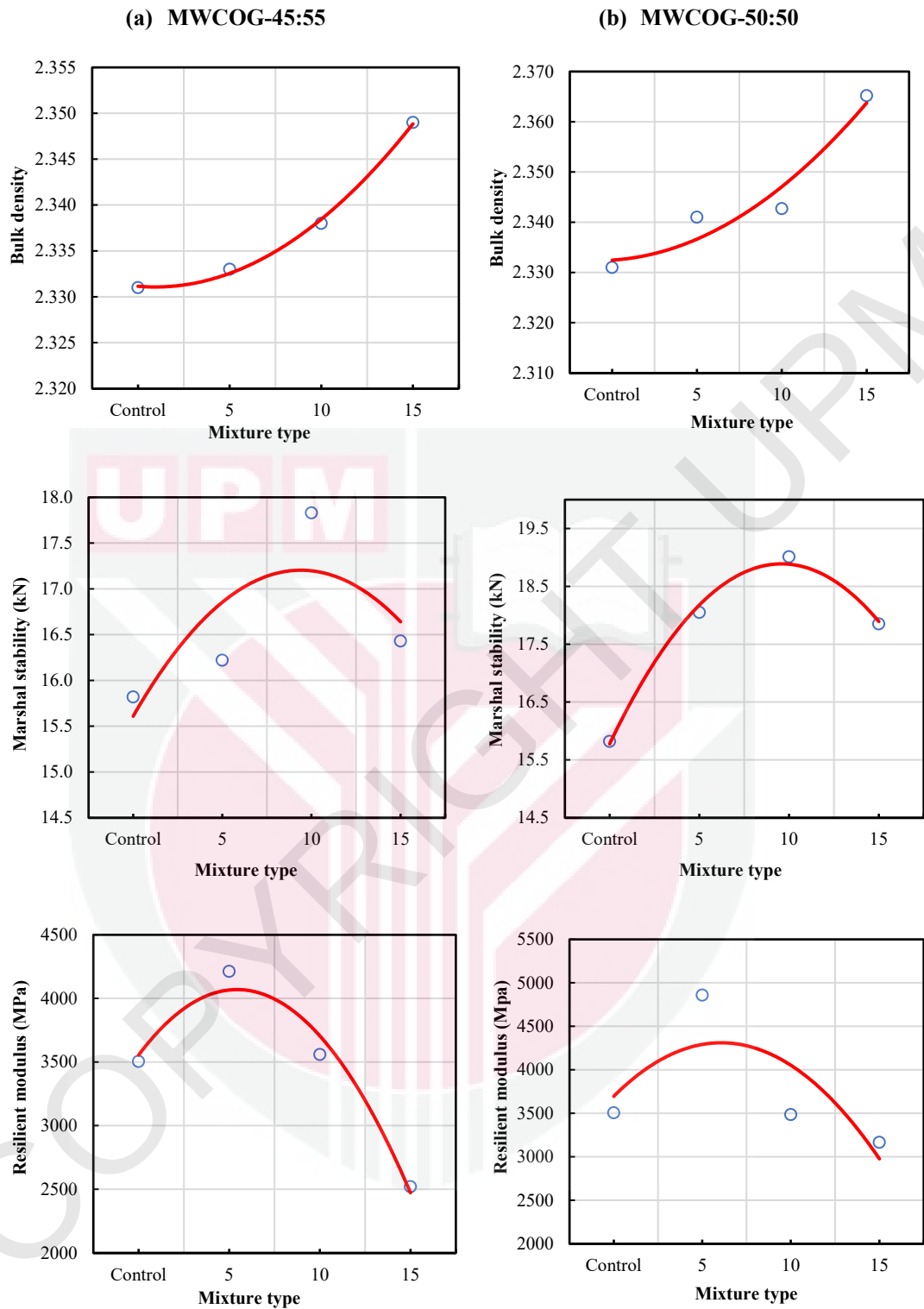


Figure 4.50: Volumetric properties of seven mixtures at OBC

4.12.4 Selection of optimum bitumen content

The OBC of the seven modified asphalt mixtures was selected by adopting the Asphalt Institute method. The mean volumetric values of the triplicate specimens i.e., VTM, density, VMA, VFB and resilient modulus are plotted versus the bitumen varying content as depicted in Figure 4.49. However, the optimum bitumen content of the control mixture is calculated by taking the average of the maximum density, Marshall stability, and the bitumen content at 4% air voids. The specimen calculation of the control mixture is as follows.

$$\begin{aligned} OBC &= \frac{\text{Stability} + \text{density} + \text{Air voids} + \text{resilient modulus}}{3} \\ &= \frac{5.01 + 5.39 + 5.1 + 4.65}{4} = 5.0375 \end{aligned}$$

The OBC of all MWCOG modified asphalt mixtures are presented in Table 4.44 and Figure 4.51. It can be seen that the increasing content of the MWCOG for the bitumen modification eventually decreases the OBC of the asphalt mixtures. The variance in the OBC among the asphalt mixtures is minimal in comparison to the control mixture. However, the MWCOG-45:55 exhibits a relatively lower OBC with higher MWCOG content when compared to MWCOG-50:50. This lower OBC can be attributed to the reduced stiffness of the bitumen following modification, distinct from MWCOG-50:50. Furthermore, the increased presence of WCO within the composite material contributes to enhanced smoothness during the mixing of the mixtures. The control mixture OBC is 5.04% which is higher than 45:55-10 and 50:50-10% with 4.92% and 4.89 respectively. On the other hand, 50:50-15% has shown an OBC of 4.93% which

is higher than the other modified bitumens. The increased OBC corresponds to the enhancement in the viscosity of the bitumens which ultimately requires more bitumen content to uniformly coat the asphalt mixture. The decline in OBC with an increase in MWCOG content up to 10%, followed by an upward trend thereafter, implies that bitumen modification reaches an optimal state at 10%. In the context of asphalt mixtures, proper preparation necessitates an ample quantity of bitumen to uniformly coat the aggregates and filler during mixing. The performance of the asphalt mixture is directly correlated with the effectiveness of coating the aggregates and filler with bitumen. In conclusion, the control mixture demands an OBC of 5.04% to uniformly blend the asphalt mixture, the highest among all other modified mixtures. This enhancement highlights the overall improvement in performance due to the modification.

Table 4.44: Optimum bitumen content of seven asphalt mixtures

Mixture type	OBC (%)	Rate of decrease (%)
Control	5.04	-
45:55-5%	4.90	-2.680
45:55-10%	4.92	-2.283
45:55-15%	4.91	-2.531
50:50-5%	4.89	-2.878
50:50-10%	4.89	-2.978
50:50-15%	4.93	-2.233

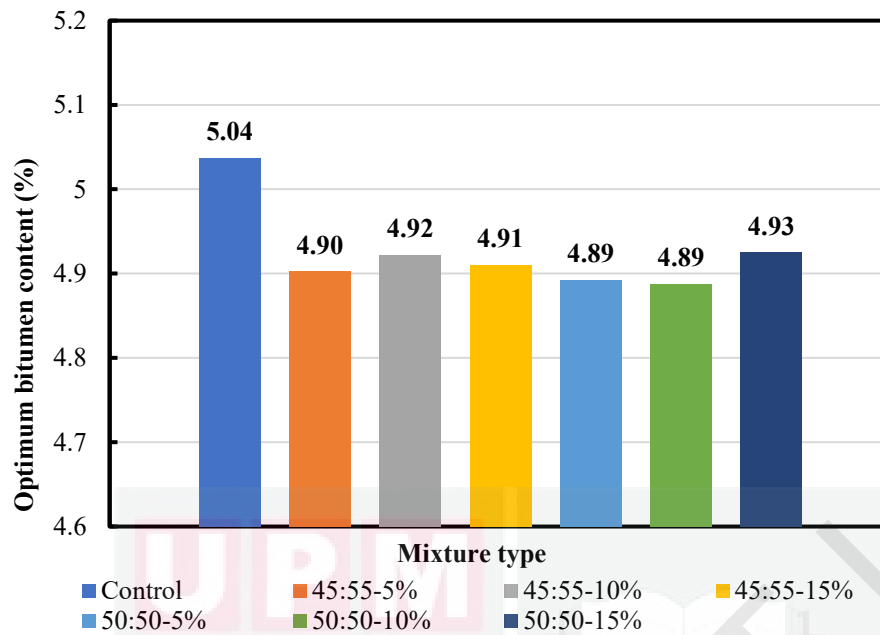


Figure 4.51: Optimum bitumen content of seven asphalt mixtures

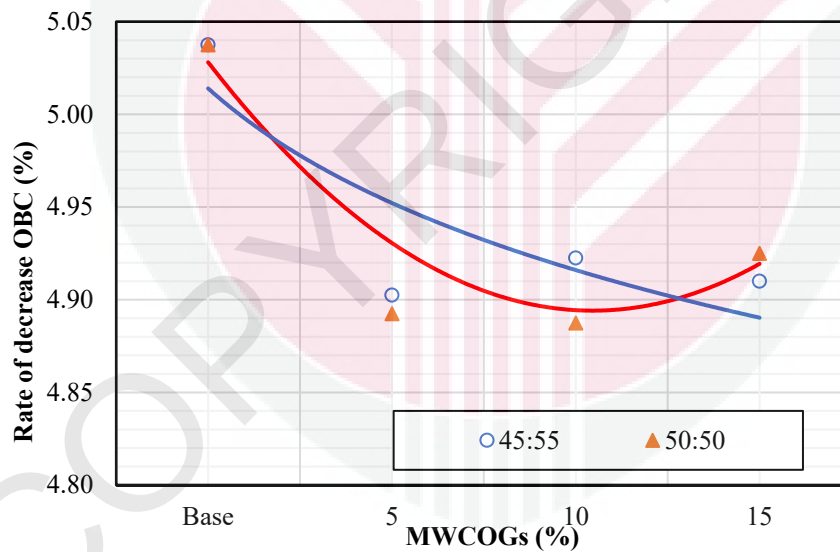


Figure 4.52: OBC rate of decrease of 45:55 and 50:50 mixtures

4.13 Summarised results of Objective 3

Following the process of elimination in objective 2 of the study, the selectively modified bitumen blends were opted for in objective 3 of the study. The outcomes

discussed in the previous sections have demonstrated a volumetric performance of the asphalt mixture incorporating the MWCOG-45:55 and MWCOG-50:50. Based on the bulk density of the asphalt mixture it is increasing on the increasing content of the MWCOGs compared to the control mixture. Whereas the Marshall stability demonstrated an improvement of up to 10% of MWCOG thenafter it is decreasing. Similarly, the stiffness of the mixture has shown an optimum performance at 5% inclusion of the MWCOGs. The results suggested that the increasing content of the MWCOG for the bitumen modification eventually decreases the OBC of the asphalt mixtures. The variance in the OBC among the asphalt mixtures is minimal in comparison to the control mixture. The control mixture OBC is 5.04% which is higher than 45:55-10% and 50:50-10% with 4.92% and 4.89% respectively. However, the MWCOG-45:55 exhibits a relatively lower OBC with higher MWCOG content when compared to MWCOG-50:50. In the subsequent objective of the study the mechanical performances of the seven asphalt mixtures would be evaluated on the determined optimum bitumen content.

4.14 Mechanical performance of asphalt mixtures (Objective 4)

In this section, the effect of the modified waste cooking oil granulate content on the mechanical performance of the asphalt mixtures has been evaluated at optimum bitumen content. The cylindrical specimens preparation and the compaction at the OBC process are the same as followed in section 4.12 for the Marshall mix design. A total of 84 Marshall specimens were compacted at air voids of 4% to evaluate the effect of MWCOG on mechanical properties. The Marshall stability and flow test, resilient modulus, rutting resistance and Cantrabro test were conducted at OBC as per the standard material testing procedures.

4.14.1 Marshall stability and flow

The modified asphalt mixture strength and the flow behaviour were evaluated following the (D1559, 1989). The triplicate of specimens for each mix design was prepared at optimum bitumen content. A total of 21 cylindrical specimens were compacted, encompassing seven mixture designs (control, 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10%, and 50:50-15%). The triplicate specimens of the modified asphalt mixture were tested for Marshall stability and flow at 60 °C. Table 4.45 and Table 4.46 provide the results of the Marshall stability and flow while graphically illustrating in Figure 4.53 and Figure 4.54 for all seven asphalt mixtures.

Table 4.45: Marshal stability results of MWCOG asphalt mixtures

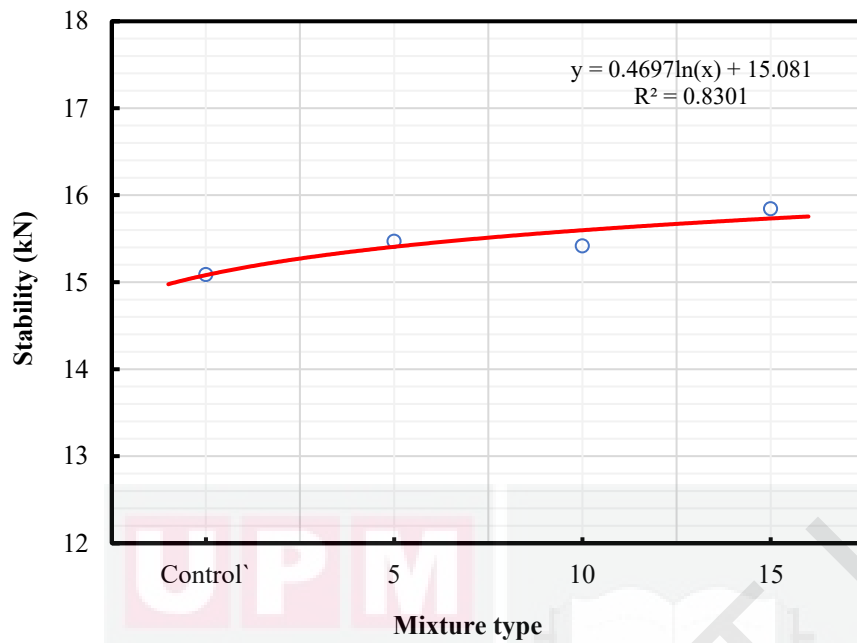
Mixture type	Marshal stability (kN)			Mean	SD
	Sample 1	Sample 2	Sample 3		
Control	15.74	15.45	14.07	15.09	0.89
45:55-5%	13.45	15.34	15.60	15.47	0.18
45:55-10%	16.30	14.12	15.83	15.42	1.15
45:55-15%	15.04	16.2	16.29	15.84	0.70
50:50-5%	14.64	15.82	16.42	15.63	0.91
50:50-10%	15.09	14.11	16.58	15.26	1.24
50:50-15%	17.12	16.04	20.27	16.58	0.76

Table 4.46: Marshal flow results of MWCOG asphalt mixtures

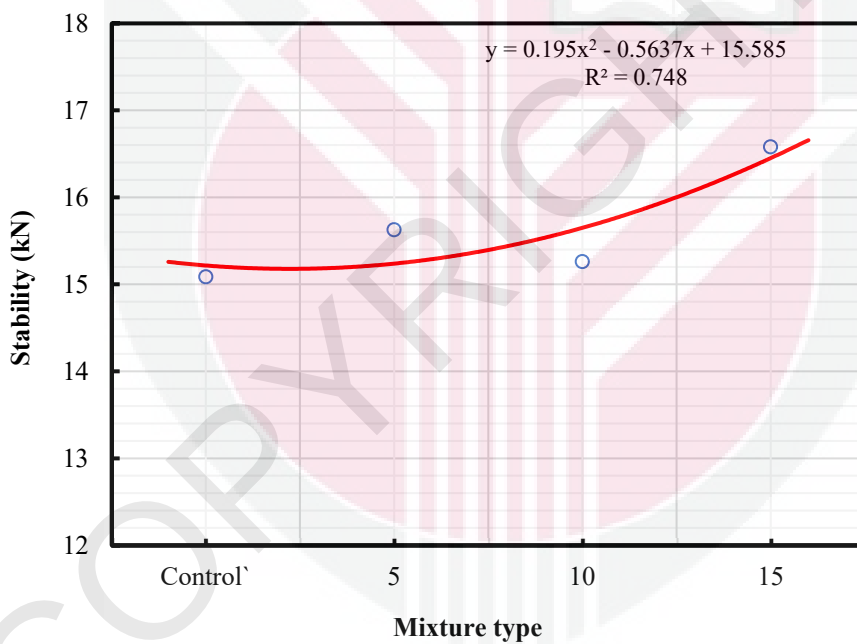
Mixture type	Flow (mm)			Mean	SD
	Sample 1	Sample 2	Sample 3		
Control	2.39	2.67	3.05	2.70	0.33
45:55-5%	2.98	3.44	3.47	3.30	0.27
45:55-10%	2.84	2.48	3.04	2.66	0.25
45:55-15%	3.52	2.46	4.41	3.46	0.75
50:50-5%	3.06	3.26	2.59	3.16	0.14
50:50-10%	3.15	3.09	2.41	2.88	0.41
50:50-15%	3.07	2.48	2.34	2.63	0.39

The findings suggest that there is a noteworthy influence of MWCOG on the Marshall stability and flow of the asphalt mixtures. The MWCOG modified asphalt mixtures

have shown a higher stability compared to the control mixtures. For instance, the stability of the 45:55-5%, 45:55-10% and 45:55-15% are 15.47 kN, 15.42 kN, and 15.84 kN respectively. However, the Marshall stability of the control mixture is 15.09 kN. Similarly, the 50:50-5%, 50:50-10% and 50:50-15% have stability of 15.63 kN, 15.26 kN and 16.58 kN respectively. Thus, the stability of 45:55-15% and 50:50-15% is 5% and 9% higher, respectively than that of the control mixture (Figure 4.53). Whereas the incorporation of MWCOG to 5% has not influenced much due to the minimal modification of asphalt mixtures, the performance of the other modified asphalt mixtures is notable. The higher stability of MWCOG-50:50 is mainly owing to the reduction in the waste cooking oil content and the increment in the SBS content with a ratio of 50:50. The results elucidate that with increasing content of MWCOG, the temperature susceptibility of modified bitumen has enhanced. Furthermore, the swelling and the initial cross-linking of the SBS before the modification process within the bitumen matrix promote the adhesion between the bitumen and SBS (Luo et al., 2022a; Zhang et al., 2019). Therefore, the addition of MWCOG to the base bitumen may have a significant impact on viscosity enhancement and ultimately improvement in the asphalt mixtures.



(a)

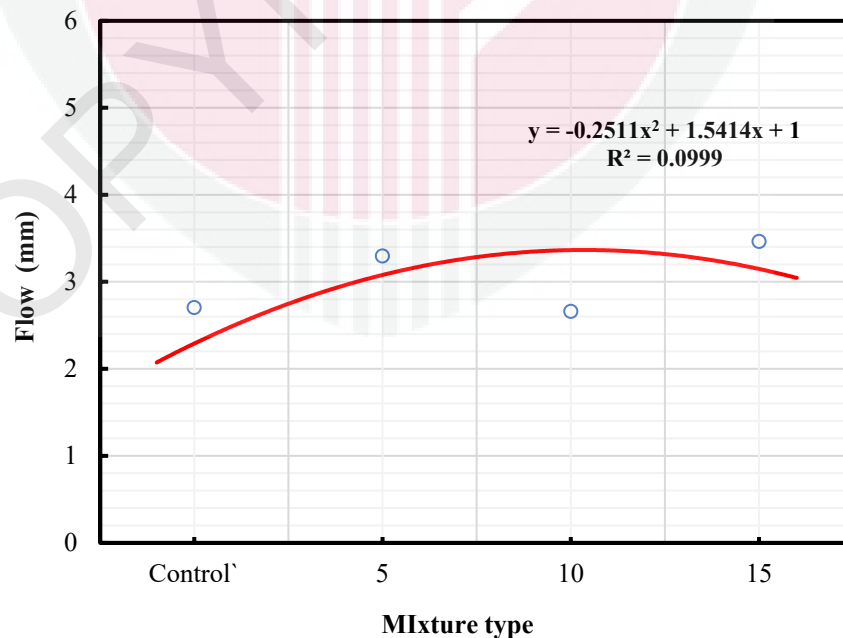


(b)

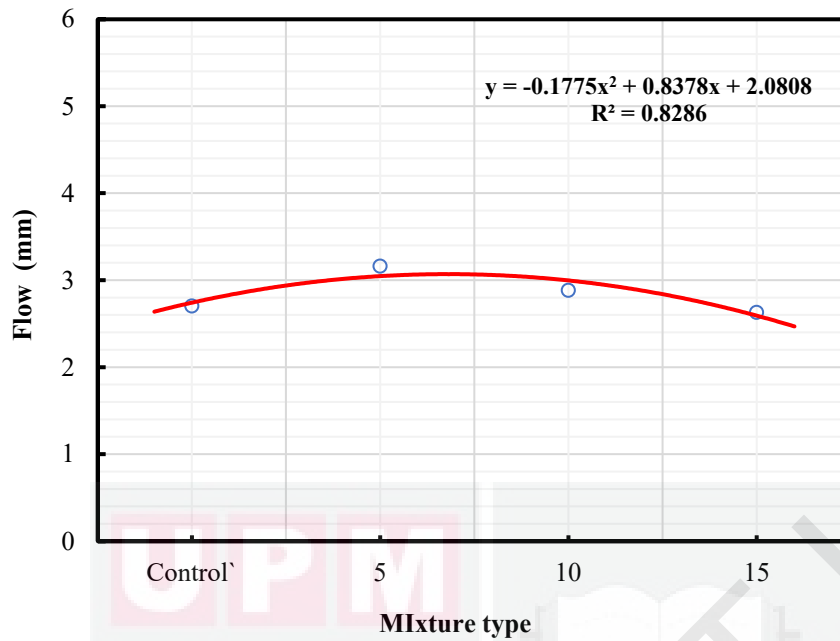
Figure 4.53: Marshal stability results of MWCOC modified mixtures: (a) 45:55 (b) 50:50

On the other hand, the flow performance of the asphalt mixtures has minimal variability compared to that of the control mixture. The lower flow values are desirable for better-performing asphalt mixtures. It can be observed from the results that by

increasing the content of the MWCOG the flow values are increasing minimally compared to the control mixture (Figure 4.54). However, the 45:55-10% and 50:50-15% demonstrated a decrease in values with 2.66 mm and 2.63 mm respectively compared to 2.70 mm of the control asphalt mixture. Whereas the 45:55-5%, 45:55-15%, 50:50-5% and 50:50-10% have shown a minimal decrease of 3.30 mm, 3.46 mm, 3.16 mm and 2.88 mm respectively. Although the variations in flow results analysis are marginal and within the standard requirements of (3-5%) (JKR, 2008). The findings suggest that 10% is the optimum content for the enhanced plastic flow of the modified asphalt mixtures. The lower content does not have any significant influence on the properties. Whereas the higher content of the MWCOG which mainly comprises the higher quantity of the WCO is affecting the asphalt mixture flow properties. Therefore, the optimum best-performing asphalt mixture in terms of Marshall stability and flow are 45:55-10% and 50:50-10%.



(a)



(b)

Figure 4.54: Marshal flow results of MWCOG modified mixtures: (a) 45:55 (b) 50:50

Table 4.47: Marshal stability and flow results of asphalt mixtures

Mixture type	OBC (%)	Stability (kN)	Flow (mm)	Marshall Quotient (kN/mm)	Percentage difference (%)	
					Stability	Flow
Control	5.03	15.1	2.7	5.58	-	-
45:55-5%	4.90	15.5	3.3	4.69	2.54	21.95
45:55-10%	4.92	15.4	2.7	5.80	2.19	-1.60
45:55-15%	4.91	15.8	3.5	4.57	5.02	28.11
50:50-5%	4.89	15.6	3.2	4.95	3.58	16.89
50:50-10%	4.88	15.3	2.9	5.29	1.15	6.66
50:50-15%	4.92	16.6	2.6	6.30	9.90	-2.71

4.14.2 Resilient modulus (M_R)

The resilient modulus test assesses the stiffness of asphalt mixtures. It's a non-destructive method measuring the modulus of elasticity, indicating the extent to which the asphalt mixture reverts to its original form within the elastic range under applied loading conditions. The Marshall cylindrical specimens underwent testing at 25°C and

40°C, following the testing parameters specified by the JKR. The results of the resilient modulus at temperatures 25°C and 40°C are provided in Table 4.48 and Table 4.49 and graphically illustrated in Figure 4.55 and Figure 4.56.

Table 4.48: Resilient modulus of asphalt mixture at 25 °C

Resilient modulus @ 25 °C (MPa)					
Mixture type	Sample 1	Sample 2	Sample 3	Mean	SD
Control	3394	3227	3460	3360	120.09
45:55-5%	2919	3651	3972	3812	226.98
45:55-10%	2518	3123	2782	2808	303.32
45:55-15%	2131	2249	1795	2058	235.56
50:50-5%	3458	3273	3381	3371	92.93
50:50-10%	2152	2965	3211	3088	173.95
50:50-15%	1856	2223	1891	1990	202.54

Table 4.49: Resilient modulus of asphalt mixture at 40 °C

Resilient modulus @ 40 °C (MPa)					
Mixture type	Sample 1	Sample 2	Sample 3	Mean	SD
Control	843	834	780	819	27.82
45:55-5%	960	920	995	958	30.64
45:55-10%	704	787	780	757	37.58
45:55-15%	691	660	701	684	17.45
50:50-5%	902	946	890	913	24.07
50:50-10%	902	991	1074	989	70.23
50:50-15%	610	634	590	611	17.98

It can be observed from the outcomes that there is no impressive enhancement in the overall stiffness of asphalt mixtures on the incorporation of the MWOCGs. However, the 45:55-5% and 50:50-5% have demonstrated an improvement of 13.5% and 0.33% respectively. The control mixture mean M_R is 3360 Mpa which is higher than the 45:55-10%, 45:55-15%, 50:50-10% and 50:50-15% with M_R of 2808 Mpa, 2058 Mpa, 3088 Mpa and 1990 Mpa respectively (Figure 4.55). It is revealed that MWCOG-45:55 have an overall minimum resilient modulus compared to that of the MWCOG-50:50. The higher concentration of the WCO within the composite material affects the stiffness properties of modified asphalt mixtures. The resilient modulus of >2500 Mpa is desirable for the AC14 asphalt mixtures following the specification of the JKR. In

general, the 45:55-15% and 50:50-15% have not satisfied the minimum criterion of 2500 Mpa. These findings are in agreement with the earlier discussed results of Marshall stability and the flow. Similar behaviour on the incorporation of the WCO directly into the asphalt mixture has been observed where higher concentrations have significantly influenced the stiffness properties of asphalt mixtures with a clear indication of loss of adhesion and higher elasticity of the material with variation in the adhesive properties of bitumen (Azahar et al., 2016c; Wang et al., 2018).

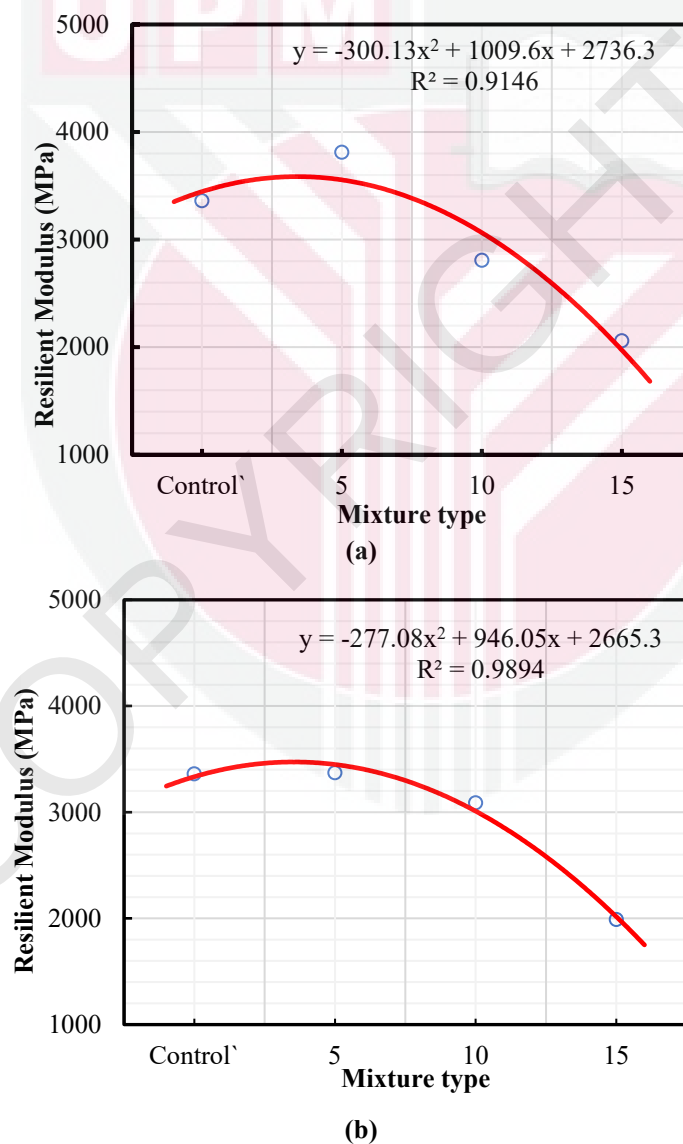


Figure 4.55: Resilient modulus results of MWCOG modified mixtures at 25 °C:
(a) 45:55 (b) 50:50

Furthermore, the resilient modulus results at a temperature of 40°C is depicted in Figure 4.56. The relationship between resilient modulus and temperature shows an inverse correlation, where an increase in temperature leads to a reduction in the resilient modulus of the asphalt mixtures regardless of the MWCOG content. The M_R of the control mixture at 40°C is 819 Mpa which is 75% lower than the control asphalt mixture at 25°C (3360 Mpa). The performance of asphalt mixtures at 40°C with higher concentrations of MWCOG is similarly inferior to their performance at 25°C. The likewise trends of M_R have been observed in incorporating the MWCOG. For instance, the 45:55-5%, 50:50-5%, and 50:50-10% have demonstrated higher resilient moduli of 958 Mpa, 913 Mpa, and 989 Mpa, respectively, compared to the control and other modified asphalt mixtures at varying MWCOG content. The improvement is due to the dissolution of WCO that promotes the SBS's swelling and homogenous distribution and thus strengthens the cross-linked network of SBS polymers within the bitumen matrix (Dong et al., 2019). The findings suggest that higher MWOCGs content is not conducive to achieving optimal performance in asphalt mixtures. Increased MWOCGs percentage significantly reduces the M_R of the asphalt mixtures and causes the soft layer on the top of the bitumen which further causes disparities in the performance. Table 4.50 provides the percentage difference between the MWCOG-45:55 and MWCOG-50:50 modified asphalt mixture. It is implied that the 45:55-5% and 50:50-5% performance is improved by 13.43 % and 0.31% respectively compared to the control mixtures.

Table 4.50: Percentage differences in resilient modulus of 45:55 and 50:50 mixtures

Mixture type	Mean Resilient modulus (MPa)		Percentage difference (%)	
	25 °C	40 °C	25 °C	40 °C
Control	3360	819	-	-
45:55-5%	3812	958	13.43	17.01
45:55-10%	2808	757	-16.45	-7.57
45:55-15%	2058	684	-38.75	-16.48
50:50-5%	3371	913	0.31	11.44
50:50-10%	3088	989	-8.10	20.76
50:50-15%	1990	611	-40.78	-25.36

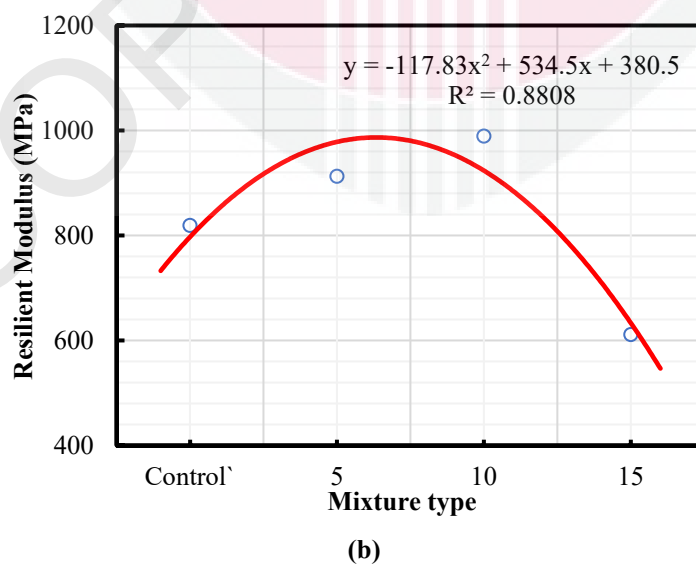
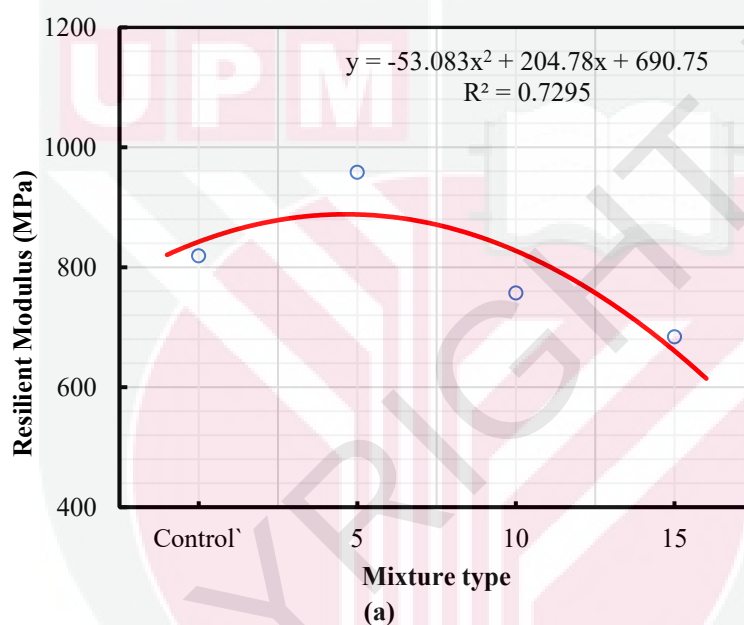


Figure 4.56: Resilient modulus results of MWCOG modified mixtures at 40 °C:
(a) 45:55 (b) 50:50

4.14.3 Rutting/Dynamic creep

The evaluation of asphalt mixtures for rutting resistance was conducted using the cyclic loading system following (EN-12697-25, 2012). Dynamic creep testing involved utilizing compacted cylindrical specimens at the Optimum Bitumen Content (OBC), with three replicates for each modified asphalt mixture. The specimens were pre-conditioned at 40°C for two hours before being subjected to loading. The seven asphalt mixtures including the control mixture (control, 45:55-5%, 45:55-10%, 45:55-15%, 50:50-5%, 50:50-10% and 50:50-15%) were tested for rutting resistance under dynamic cyclic loading. Table 4.51 presents the measured test results, showcasing strain (%), minimum strain rate, and strain at 3600 cycles. These findings are graphically depicted in Figure 4.57 to Figure 4.59.

Table 4.51: Dynamic creep test results of five asphalt mixtures

Mixture type	Strain (%) @ min strain rate	Minimum strain rate ($\mu\epsilon$ /cycle)	Cycles @ min strain rate	Cumulative strain (%) @ 3600 cycles
Control	0.61	0.1	3244	0.63
45:55-5%	0.35	0.21	3073	0.46
45:55-10%	0.5	0.31	2220	0.54
45:55-15%	0.72	0.1	2441	0.75
50:50-5%	0.48	0.11	2085	0.54
50:50-10%	0.61	0.22	3061	0.62
50:50-15%	0.6	0.3	2937	0.67

Figure 4.57 depicts the cumulative strains of the modified asphalt mixtures using MWCOG-45:55 and MWCOG-50:50 respectively. It can be seen that the strain of the MWCOG modified asphalt mixture at 3600 cycles showcases the decreasing trend of increasing the content of MWCOG. As expected, the strain is increasing on the higher content of the MWCOG. The 45:55-5% and 45:55-10% have a strain value of 0.46% and 0.54% which is lower than the 0.63% of the control mixtures. Similarly, the 50:50-

5% and 50:50-10% reduced the strain to 0.54% and 0.62%. However, the 45:55-15% and 50:50-15% asphalt mixtures display a higher strain of 0.75% and 0.67% respectively under dynamic loading. The higher strain corresponds to the higher quantity of the WCO within the asphalt mixture. The WCO higher concentration causes a reduction in the stiffness and the elasticity of the bitumen which ultimately affects the resistance against the rutting.

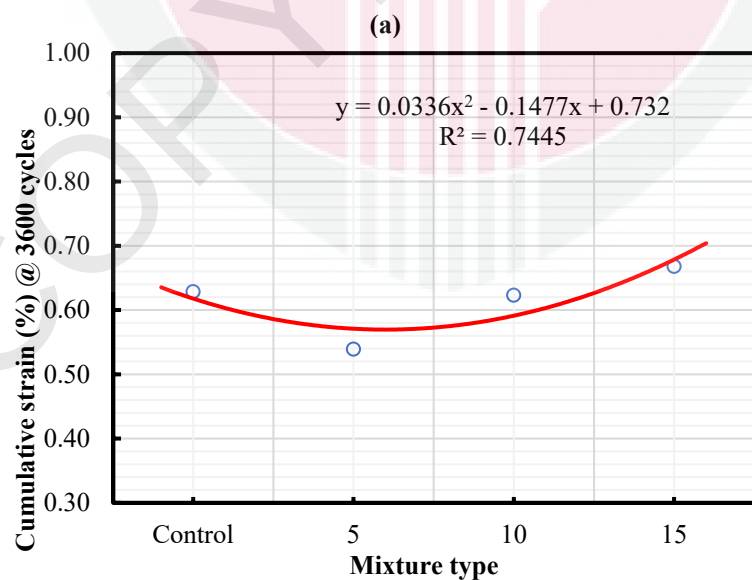
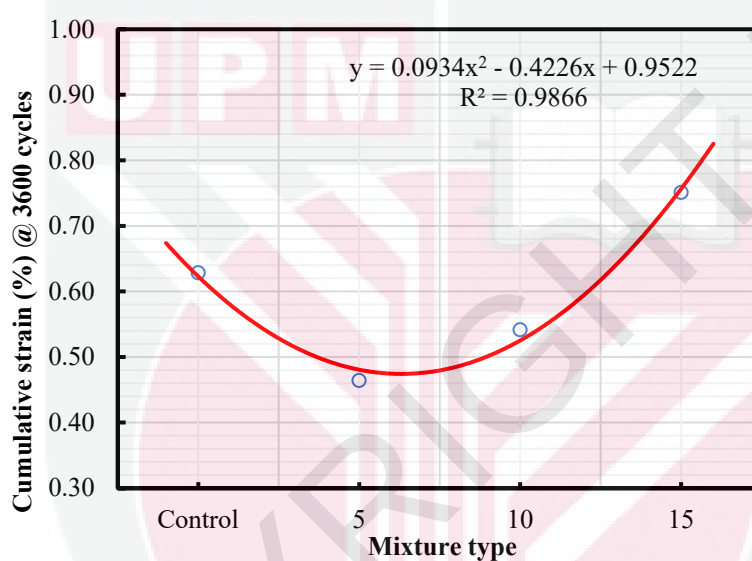


Figure 4.57: Cumulative strain (%) of modified asphalt mixture: (a) 45:55 (b) and 50:50 at 3600 cycles

Figure 4.58 and Figure 4.59 illustrate the total permanent strain (%) of the MWCOG-45:55 and MWCOG-50:50 modified asphalt mixture respectively. The slope of each asphalt mixture at zone-I and zone-II of the curves is provided in Table 4.52. The outcomes imply that the total permanent strain of 45:55-5% and 50:50-5% displays the lower strain on each cycle with lower slope values compared to the control mixture. The lower slope values of the total permanent strain line are desirable which shows the enhancement in resistance against the rutting and vice versa. As probable, SBS imparts stiffening characteristics to bitumen, thereby decreasing the strain of the modified asphalt mixtures. The slope at zone-I is higher than the zone-II of all the modified mixtures. The reason for the highest slope at zone-I is an initial settlement of the specimens which reflects the sudden rise in the strain. Whereas zone-II demonstrates minor variations in a strain of asphalt mixtures as the strain has already dropped notably compared to that of zone-I. Interestingly, the 45:55-15% and 50:50-15% display the highest strain even compared to the control mixture.

Table 4.52: Slope (%) of all asphalt mixtures at zone-I and zone-II

Mixture type	Slope (%)	
	Zone-I	Zone-II
Control	0.0008	0.00006
45:55-5%	0.0006	0.00005
45:55-10%	0.0007	0.00005
45:55-15%	0.0009	0.00006
50:50-5%	0.0007	0.00006
50:50-10%	0.0008	0.00005
50:50-15%	0.0009	0.00006

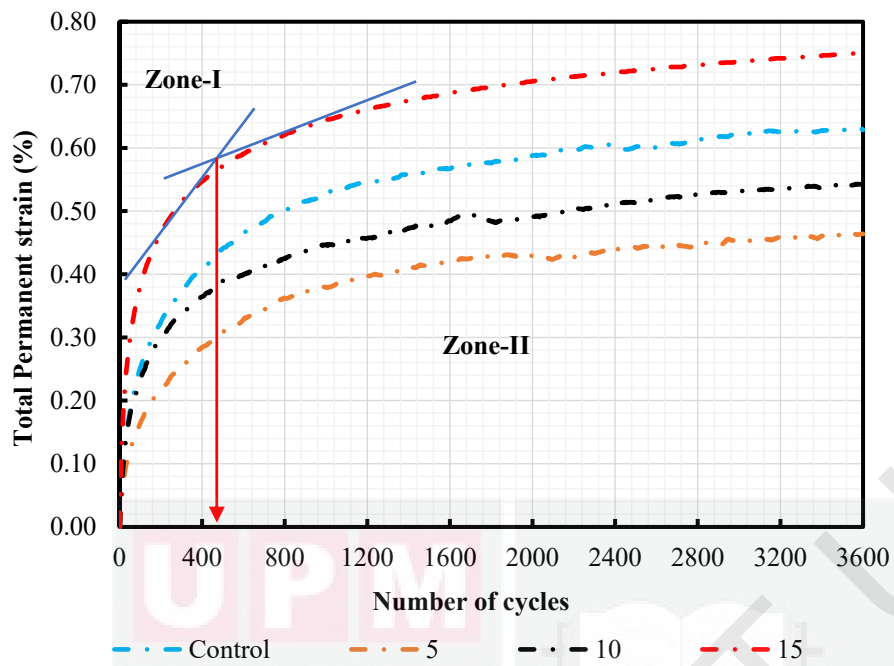


Figure 4.58: Total permanent strain (%) versus number of cycles of 45:55 asphalt mixtures

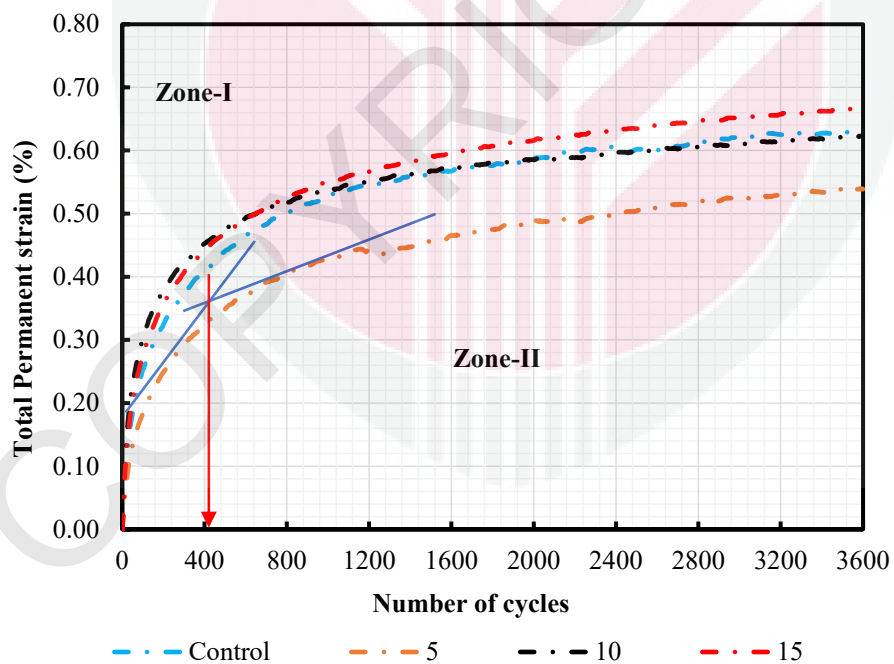


Figure 4.59: Total permanent strain (%) versus number of cycles of 50:50 asphalt mixtures

Furthermore, the seven asphalt mixtures' creep modulus and the creep rate at the 3600 cycles were determined using the equations (3.12 and 3.13). The summarised results of the creep modulus and creep rate are presented in Table 4.53 and graphically illustrated in Figure 4.60 and Figure 4.61. The asphalt mixtures mainly require a higher creep modulus and a lower creep rate to perform better under various loading conditions. The higher creep modulus reflects the strong and durable asphalt mixture whereas the lower creep rate is desirable for the high amount of the energy absorbance during the dynamic loading (Safaeldeen et al., 2022).

Table 4.53: Creep modulus and creep rate of asphalt mixtures

Mixture type	Creep modulus (Mpa)	Creep rate ($\mu\epsilon/\text{cycle}$)	Marginal change (%)	
			Creep modulus	Creep rate
Control	239	0.000029	-	-
45:55-5%	323	0.000021	35.15	-27.59
45:55-10%	277	0.000022	15.90	-24.14
45:55-15%	200	0.000034	-16.32	17.24
50:50-5%	278	0.000025	16.32	-13.79
50:50-10%	241	0.000023	0.84	-20.69
50:50-15%	225	0.000034	-5.86	17.24

Figure 4.60 display the creep modulus of the MWCOG-45:55 and MWCOG-50:50 modified asphalt mixtures respectively. It is revealed that the control mixture has demonstrated a lower creep modulus of 239 Mpa which is lower than the creep modulus of 45:55-5% and 45:55-10% with values of 323 Mpa and 277 Mpa respectively. Similarly, the 50:50-5% and 50:50-10% MWCOG modified asphalt mixtures have displayed 278 Mpa and 241 Mpa respectively. Moreover, the overall improvement of 45:55-5% and 45:55-10% is 35.15% and 15.90% respectively. Whereas the 50:50-5% and 50:50-10% have shown a 16.32% and 0.84% enhancement respectively. As expected, the 45:55-15% and 50:50-15% have lower stiffness

modulus of 200 Mpa and 225 Mpa respectively. The decrease in creep stiffness modulus at higher MWCOG content is attributed to the increased concentration of WCO within the asphalt matrix. The higher content causes the softening of the bitumen which ultimately reduces the resistance against the rutting. The findings of the MWCOG modified asphalt mixtures in terms of the stiffness modulus satisfy the minimum criterion of ≥ 75 Mpa as per the JKR specimens. The creep stiffness modulus of 200 MPa exhibited by 50:50-15% surpasses the minimum criteria, indicating strong performance. These results correlate with strain values, where lower strain corresponds to higher creep stiffness modulus, and vice versa. It can be observed that the overall performance of the MWCOG-45:55 is promising at the lower content of the MWCOG. Azahar et al. (2017) and Luo et al. (2022b) concluded similar outcomes on incorporating the WCO and SBS on varying content.

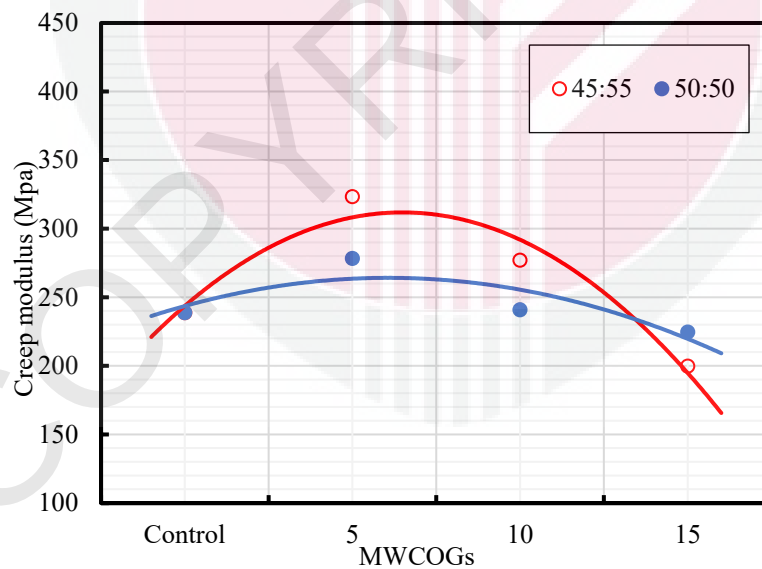


Figure 4.60: Comparative assessment of 45:55 and 50:50 creep modulus

Moreover, the creep rate of the seven asphalt mixtures exhibits an inverse relationship with the creep modulus. The results are provided in Table 4.52 and Figure 4.61. The

45:55-5% and 45:55-10% modified asphalt mixture has displayed an improvement of 27% and 24% with creep rate values of 0.00021 and 0.00022 in comparison to the control mixture (0.00029) respectively. Similarly, the performance of the MWCOG-50:50 asphalt mixture is likewise to the results of the creep modulus. The 50:50-5% and 50:50-10% achieved 0.00025 and 0.00023 with 13% and 20% improvement compared to the control mixture. The enhanced performance of the asphalt mixtures can be attributed to the MWCOG, combining SBS and WCO. This combination enhances the bitumen's viscoelastic response, consequently impacting the stiffness observed in the asphalt mixtures. The asphalt mixtures of 45:55-5% and 50:50-5% exhibit notable performance in terms of both creep rate and creep stiffness modulus, showcasing their promising characteristics. In summary, the enhanced performance of the MWCOG-modified asphalt mixtures can be attributed to the improved adhesion and viscoelastic properties of the bitumen. This improvement results in more durable and strong asphalt mixtures, characterized by reduced strain and higher creep modulus.

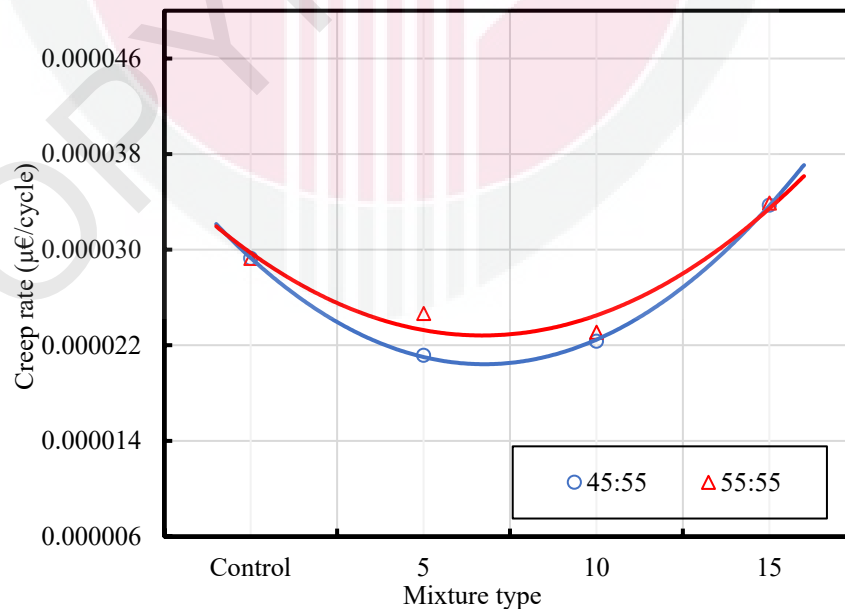


Figure 4.61: Comparative assessment of 45:55 and 50:50 creep rate

4.14.4 Cantrabro test

The durability, resistance to disintegration and cohesion loss of the asphalt mixture is assessed through the Cantabro test. The dense graded asphalt mixture's durability is an important factor in the long service life of flexible pavements. A practical and feasible testing method is necessary to assess these concern properties. Therefore, the Cantabro test appears to be a promising evaluation method to meet these requirements. The 21 cylindrical specimens from the seven asphalt mixtures, each prepared at the OBC, were tested for the Cantabro test to determine the cohesion or stone loss. For each mixture type, triplicate specimens were tested to ensure the accuracy and reliability of the data following (ASTM C-131) and JKR specifications. The detailed procedure and parameters are discussed in Chapter 3. Table 4.54 presented the results of MWCOG-45:55 and MWCOG-50:50 before and after the testing process whereas graphically depicted in Figure 4.62 to Figure 4.64.

Table 4.54: Cantrabro test results of MWCOG asphalt mixtures

Mixture type	Wt before test (g)	Wt after test (g)	Average loss (%)	Loss change (%)
Control	1194.27	1164.47	2.50	-
45:55-5%	1193.43	1173.33	1.68	-32.8
45:55-10%	1196.77	1181.43	1.28	-48.8
45:55-15%	1194.93	1183.30	0.97	-61.2
50:50-5%	1192.07	1162.63	2.47	-1.2
50:50-10%	1197.60	1183.27	1.20	-52
50:50-15%	1195.67	1180.67	1.25	-50

It is elucidated that the asphalt mixture modification with MWCOG improves the overall adhesion and resistance to the integration of the aggregates. Figure 4.62 illustrates the MWCOG-45:55 modified asphalt mixtures. It can be seen that increasing the content of the MWCOG has significantly caused a reduction in the average loss of the weight of the specimens. The weight of the control specimens before the test was

1194.27 g which was reduced to 1164.47 g after 300 revolutions in the Los Angeles machine. On the contrary, the 45:55-15% and 50:50-15% modified mixture specimens' weights were 1194.93 g and 1195.65 g and decreased to 1183.30 g and 1180.67 g respectively (Figure 4.63). The findings suggest that the increasing content of MWCOG has significantly improved the durability and resistance against the integration of specimen aggregates. Moreover, the average loss of the control specimens is 2.50% which is higher among all the modified mixtures. However, the MWCOG-45:55 demonstrated an overall lower average loss compared to the MWCOG-50:50. The 45:55-15% and 50:50-15% have shown a 61% and 50% improvement in comparison to that of the control mixture. The comparative analysis of the average loss between MWCOG-45:55 and MWCOG-50:50 provides additional validation, demonstrating the superior performance of MWCOG-45:55. Meanwhile, MWCOG-50:50 also exhibit improved performance compared to the control mixture. The improved outcomes of the Cantabro test in the MWCOG-45:55 and MWCOG-50:50 mixtures can be attributed to their superior adhesion between aggregates and bitumen, a result of the modified bitumen's enhanced viscoelastic behaviours. The incorporation of waste cooking oil and SBS likely enhances elasticity and interfacial bonding within the composite. This enhanced adhesion potentially strengthens the mixture against disintegration, increases overall cohesion, and contributes to promising performance compared to the control mixture.

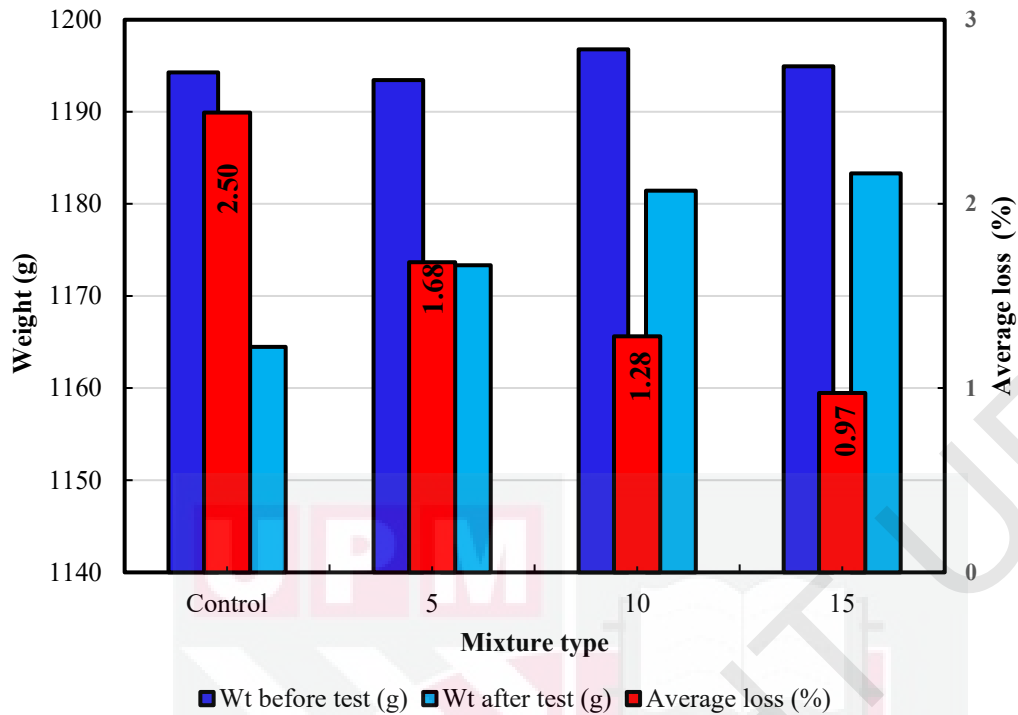


Figure 4.62: Cantrabro test results of asphalt mixtures 45:55

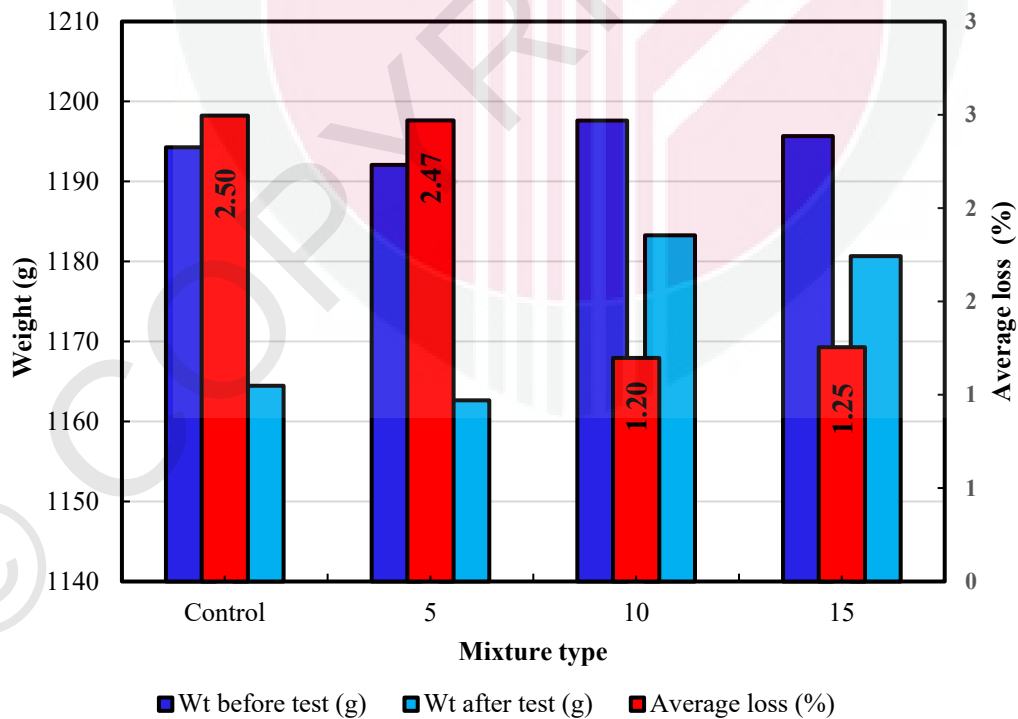


Figure 4.63: Cantrabro test results of asphalt mixtures 50:50

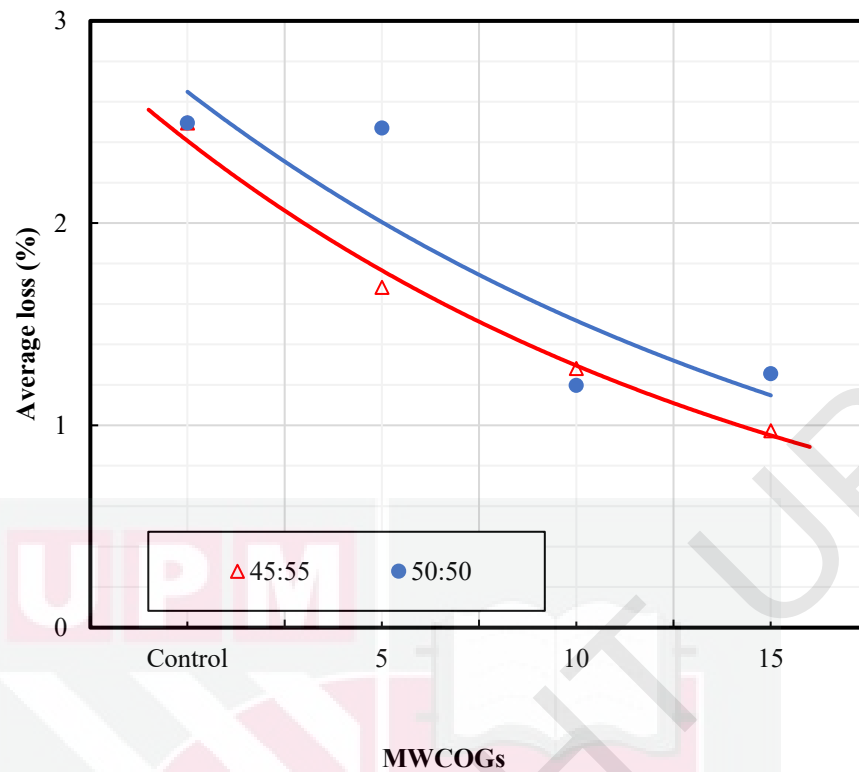


Figure 4.64: Comparative assessment of average loss of 45:55 and 50:50 mixtures

4.15 Two-way ANOVA analysis

The statistical analysis of the waste cooking oil modified bitumen with the incorporation of the MWCOG was evaluated by adopting the two-way ANOVA analysis followed by the post hoc multiple comparison with Tukey method. The ten MWCOG modified bitumen blends are analysed for the rotational viscosity and the complex modulus whereas six modified asphalt mixtures are analysed for Marshall stability and the resilient modulus. The ANOVA followed by the multiple comparison provides the framework to test the hypothesis that the WCO modification affects the performance of the bitumen and the asphalt mixtures. The succeeding section provides the results of MWCOG bitumen and asphalt mixtures two-way ANOVA and the post hoc analysis.

4.15.1 MWCOGs bitumen

The two-way ANOVA results for rotational viscosity are presented in Table 4.55. The results indicate that the model's overall fit is highly significant ($F = 293.848$, $p < 0.005$), demonstrating that at least one of the independent factors has a significant effect on the dependent variable. However, the main effect of Blends_Type was not significant ($F = 0.538$, $p = 0.472$), suggesting that the different levels of Blends_Type did not significantly impact the viscosity. The primary cause of the difference in the mean viscosity values was found to be MWCO_Percent, with significant results ($F = 326.494$, $p < 0.005$). Thus, we reject the null hypothesis, concluding that MWCO_Percent significantly affects rotational viscosity, explaining approximately 99% of the variability (Adjusted R-squared = 0.990). In contrast, the two-way ANOVA results for complex modulus are displayed in Table 4.56 also demonstrate a significant model fit ($F = 12.759$, $p < 0.005$). However, the Blends_Type was found to be significant ($F = 46.692$, $p < 0.005$), indicating a substantial impact on the complex modulus, alongside MWCO_Percent, which also showed significant effects ($F = 8.083$, $p < 0.005$). Therefore, the null hypothesis is rejected for both factors in this case, and the model explains approximately 80% of the variability in complex modulus (Adjusted R-squared = 0.802). In conclusion, Blends_Type significantly influenced complex modulus, whereas it did not affect rotational viscosity. In contrast, MWCO_Percent demonstrated a significant impact on both properties.

Table 4.55: Two way ANOVA rotational viscosity

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	29265364.283 ^a	10	2926536.428	293.848	.000
Intercept	82773941.920	1	82773941.920	8311.185	.000
Blends_Type	5360.040	1	5360.040	.538	.472
MWCO_Percent	29264989.043	9	3251665.449	326.494	.000
Error	189227.527	19	9959.344		
Total	112228533.73	30			
Corrected Total	29454591.810	29			

a R Squared = .994 (Adjusted R Squared = .990)

Table 4.56: Two way ANOVA complex modulus

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	44461924.583 ^a	10	4446192.458	12.759	.000
Intercept	311664100.833	1	311664100.83	894.376	.000
Blends_Type	16270833.750	1	16270833.750	46.692	.000
MWCO_Percent	25349823.750	9	2816647.083	8.083	.000
Error	6620949.583	19	348471.031		
Total	362746975.00	30			
Corrected Total	51082874.167	29			

a R Squared = .870 (Adjusted R Squared = .802)

The post hoc multiple comparison results for rotational viscosity and complex modulus, presented in Table 4.57 and Table 4.58 respectively, were conducted to assess the differences between various levels of the independent variable "MWCO_Percent," while the Blends_Type variable was excluded from the analysis since it only has two levels. Significant differences are marked with an asterisk (*) at $p = 0.05$. In Table 4.57, the rotational viscosity results show a significant increase as WCO content rises. For example, the 45:55 blend at 25% WCO shows a mean difference of -2998.9333 ($p = 0.000$) compared to the 5% WCO blend, while the 50:50 blend at 25% WCO also demonstrates a significant increase in viscosity, with a mean difference of -2609.9333 ($p = 0.000$) compared to the 50:50_5% blend.

Table 4.57: Post hoc multiple comparisons of rotational viscosity

(I) MWCO_Percent	(J) MWCO_Percent	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
45:55_5%	45:55_10%	-292.9667*	81.48351	.007	-583.2127	-2.7207
	45:55_15%	-836.7000*	81.48351	.000	-1126.9460	-546.4540
	45:55_20%	-1474.2333*	81.48351	.000	-1764.4793	-1183.9873
	45:55_25%	-2998.9333*	81.48351	.000	-3289.1793	-2708.6873
	50:50_5%	-48.7000	81.48351	1.00	-338.9460	241.5460
	50:50_10%	-432.6667*	81.48351	.001	-722.9127	-142.4207
	50:50_15%	-1169.4667*	81.48351	.000	-1459.7127	-879.2207
	50:50_20%	-1614.0333*	81.48351	.000	-1904.2793	-1323.7873
	50:50_25%	-2609.9333*	81.48351	.000	-2900.1793	-2319.6873
	45:55_15%	-543.7333*	81.48351	.000	-833.9793	-253.4873
45:55_10%	45:55_20%	-1181.2667*	81.48351	.000	-1471.5127	-891.0207
	45:55_25%	-2705.9667*	81.48351	.000	-2996.2127	-2415.7207
	50:50_5%	244.2667	81.48351	.145	-45.9793	534.5127
	50:50_10%	-139.7000	81.48351	.775	-429.9460	150.5460
	50:50_15%	-876.5000*	81.48351	.000	-1166.7460	-586.2540
	50:50_20%	-1321.0667*	81.48351	.000	-1611.3127	-1030.8207
	50:50_25%	-2316.9667*	81.48351	.000	-2607.2127	-2026.7207

Table 4.57: Continued

45:55_15%	45:55_20%	-637.5333*	81.48351	.000	-927.7793	-347.2873
	45:55_25%	-2162.2333*	81.48351	.000	-2452.4793	-1871.9873
	50:50_5%	788.0000*	81.48351	.000	497.7540	1078.2460
	50:50_10%	404.0333*	81.48351	.003	113.7873	694.2793
	50:50_15%	-332.7667*	81.48351	.017	-623.0127	-42.5207
	50:50_20%	-777.3333*	81.48351	.000	-1067.5793	-487.0873
45:55_20%	50:50_25%	-1773.2333*	81.48351	.000	-2063.4793	-1482.9873
	45:55_25%	-1524.7000*	81.48351	.000	-1814.9460	-1234.4540
	50:50_5%	1425.5333*	81.48351	.000	1135.2873	1715.7793
	50:50_10%	1041.5667*	81.48351	.000	751.3207	1331.8127
	50:50_15%	304.7667*	81.48351	.035	14.5207	595.0127
	50:50_20%	-139.8000	81.48351	.775	-430.0460	150.4460
45:55_25%	50:50_25%	-1135.7000*	81.48351	.000	-1425.9460	-845.4540
	50:50_5%	2950.2333*	81.48351	.000	2659.9873	3240.4793
	50:50_10%	2566.2667*	81.48351	.000	2276.0207	2856.5127
	50:50_15%	1829.4667*	81.48351	.000	1539.2207	2119.7127
	50:50_20%	1384.9000*	81.48351	.000	1094.6540	1675.1460
	50:50_25%	389.0000*	81.48351	.004	98.7540	679.2460
50:50_5%	50:50_10%	-383.9667*	81.48351	.005	-674.2127	-93.7207
	50:50_15%	-1120.7667*	81.48351	.000	-1411.0127	-830.5207
	50:50_20%	-1565.3333*	81.48351	.000	-1855.5793	-1275.0873
	50:50_25%	-2561.2333*	81.48351	.000	-2851.4793	-2270.9873
50:50_10%	50:50_15%	-736.8000*	81.48351	.000	-1027.0460	-446.5540
	50:50_20%	-1181.3667*	81.48351	.000	-1471.6127	-891.1207
	50:50_25%	-2177.2667*	81.48351	.000	-2467.5127	-1887.0207
50:50_15%	50:50_20%	-444.5667*	81.48351	.001	-734.8127	-154.3207
	50:50_25%	-1440.4667*	81.48351	.000	-1730.7127	-1150.2207
50:50_20%	50:50_25%	-995.9000*	81.48351	.000	-1286.1460	-705.6540

*. The mean difference is significant at the .05 level.

These findings suggest that higher WCO content leads to greater resistance to flow in the modified bitumen, improving its performance for road applications. Similarly, Table 4.58 shows that the complex modulus increases significantly with higher WCO content, reflecting enhanced stiffness and deformation resistance. For instance, the 45:55 blend at 25% WCO shows a significant increase in modulus compared to the 5% blend, with a mean difference of -2286.6667 ($p = 0.004$), while the 50:50 blend at 25% WCO demonstrates the largest increase in modulus, with a mean difference of -3191.6667 ($p = 0.000$). These results indicate that the modified bitumen becomes stiffer and more elastic as WCO content increases, which is important for resisting deformation under heavy traffic loads. In conclusion, the findings from both the rotational viscosity and complex modulus tests confirm that increasing WCO content significantly enhances the overall performance of the modified bitumen.

The Figure 4.65 and Figure 4.66 illustrate the estimated marginal means for rotational viscosity and complex modulus show significant improvements with increasing WCO content across the blends. For rotational viscosity, the 45:55 blend increases from 508.574 at 5% WCO to 3507 at 25% WCO, while the 50:50 blend rises from 566 to 3127 over the same range. In terms of complex modulus, the 45:55 blend's mean modulus increases from 1750.375 at 5% WCO to 4037.042 at 25% WCO, and the 50:50 blend goes from 1482.958 to 4421.292. These findings indicate that higher WCO concentrations significantly enhance both viscosity and stiffness, leading to improved performance of modified bitumen for road construction applications.

Table 4.58: Post hoc multiple comparisons of complex modulus

(I) MWCO_Percent	(J) MWCO_Percent	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
45:55_5%	45:55_10%	-1263.3333	481.98965	.003	-2980.1908	453.5242
	45:55_15%	-1651.6667	481.98965	.000	-3368.5242	65.1908
	45:55_20%	-1906.6667*	481.98965	.002	-3623.5242	-189.8092
	45:55_25%	-2286.6667*	481.98965	.004	-4003.5242	-569.8092
	50:50_5%	-253.3333	481.98965	1.000	-1970.1908	1463.5242
	50:50_10%	-1626.6667	481.98965	.000	-3343.5242	90.1908
	50:50_15%	-2375.0000*	481.98965	.003	-4091.8575	-658.1425
	50:50_20%	-2776.6667*	481.98965	.000	-4493.5242	-1059.8092
45:55_10%	45:55_15%	-388.3333	481.98965	.000	-2105.1908	1328.5242
	45:55_20%	-643.3333	481.98965	.002	-2360.1908	1073.5242
	45:55_25%	-1023.3333	481.98965	.034	-2740.1908	693.5242
	50:50_5%	1010.0000	481.98965	.000	-706.8575	2726.8575
	50:50_10%	-363.3333	481.98965	.999	-2080.1908	1353.5242
	50:50_15%	-1111.6667	481.98965	.000	-2828.5242	605.1908
	50:50_20%	-1513.3333	481.98965	.003	-3230.1908	203.5242
	50:50_25%	-1928.3333*	481.98965	.020	-3645.1908	-211.4758
45:55_15%	45:55_20%	-255.0000	481.98965	.000	-1971.8575	1461.8575
	45:55_25%	-635.0000	481.98965	.000	-2351.8575	1081.8575
	50:50_5%	1398.3333	481.98965	.007	-318.5242	3115.1908
	50:50_10%	25.0000	481.98965	1.000	-1691.8575	1741.8575
	50:50_15%	-723.3333	481.98965	.000	-2440.1908	993.5242
	50:50_20%	-1125.0000	481.98965	.002	-2841.8575	591.8575
	50:50_25%	-1540.0000	481.98965	.102	-3256.8575	176.8575
45:55_20%	45:55_25%	-380.0000	481.98965	.008	-2096.8575	1336.8575
	50:50_5%	1653.3333	481.98965	.065	-63.5242	3370.1908
	50:50_10%	280.0000	481.98965	1.000	-1436.8575	1996.8575
	50:50_15%	-468.3333	481.98965	.000	-2185.1908	1248.5242
	50:50_20%	-870.0000	481.98965	.005	-2586.8575	846.8575
	50:50_25%	-1285.0000	481.98965	.004	-3001.8575	431.8575
45:55_25%	50:50_5%	2033.3333*	481.98965	.013	316.4758	3750.1908
	50:50_10%	660.0000	481.98965	.002	-1056.8575	2376.8575
	50:50_15%	-88.3333	481.98965	1.000	-1805.1908	1628.5242
	50:50_20%	-490.0000	481.98965	.987	-2206.8575	1226.8575
	50:50_25%	-905.0000	481.98965	.003	-2621.8575	811.8575
50:50_5%	50:50_10%	-1373.3333	481.98965	.000	-3090.1908	343.5242
	50:50_15%	-2121.6667*	481.98965	.009	-3838.5242	-404.8092
	50:50_20%	-2523.3333*	481.98965	.002	-4240.1908	-806.4758
	50:50_25%	-2938.3333*	481.98965	.000	-4655.1908	-1221.4758
50:50_10%	50:50_15%	-748.3333	481.98965	.004	-2465.1908	968.5242
	50:50_20%	-1150.0000	481.98965	.000	-2866.8575	566.8575
	50:50_25%	-1565.0000	481.98965	.000	-3281.8575	151.8575
50:50_15%	50:50_20%	-401.6667	481.98965	.997	-2118.5242	1315.1908
	50:50_25%	-816.6667	481.98965	.000	-2533.5242	900.1908
50:50_20%	50:50_25%	-415.0000	481.98965	.000	-2131.8575	1301.8575

*. The mean difference is significant at the .05 level.

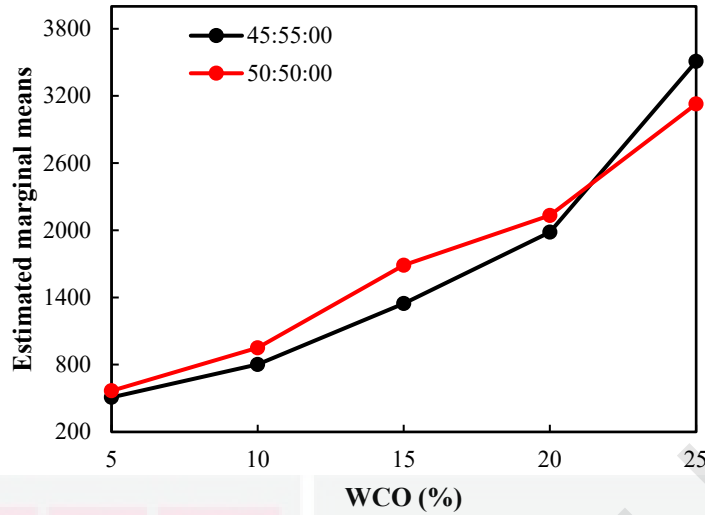


Figure 4.65: Estimated means of rotational viscosity at varying WCO%

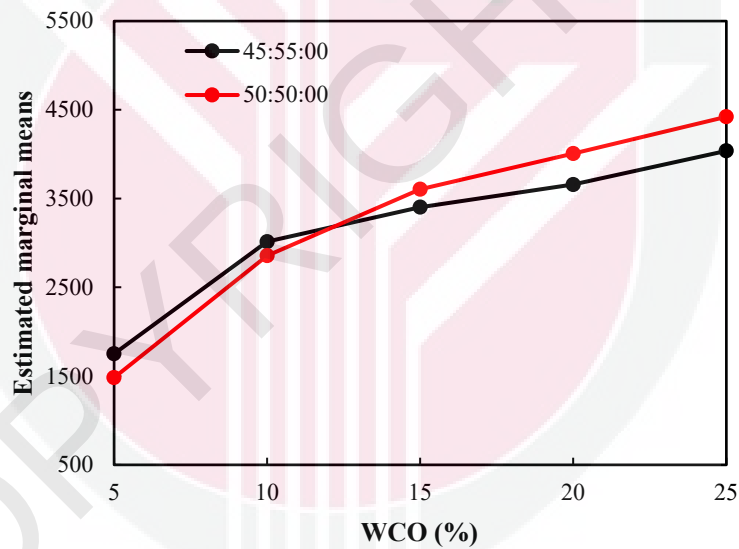


Figure 4.66: Estimated means of complex modulus at varying WCO%

4.15.2 MWCOCs asphalt mixtures

The ANOVA results of Marshall stability and resilient modulus indicates significant effects of WCO content on the mechanical properties of modified bitumen, with the results displayed in Table 4.59 and Table 4.60. The independent variable in this

analysis, MWCO_Percent, demonstrates a highly significant effect on Marshall stability, with the model fit showing an F-value of 18.250 ($p < 0.005$) and a significant effect on stability ($F = 21.300$, $p = 0.000$). In contrast, the Blends_Type factor did not exhibit a significant impact ($F = 0.525$, $p = 0.484$). Similarly, the resilient modulus analysis reveals a significant overall model fit ($F = 7.222$, $p = 0.003$), with MWCO_Percent again showing a significant effect ($F = 8.625$, $p = 0.002$), while Blends_Type remains non-significant ($F = 0.328$, $p = 0.578$).

Table 4.59: Two way ANOVA Marshall stability

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	118.890 ^a	6	19.815	18.250	.000
Intercept	5143.008	1	5143.008	4736.829	.000
Blends_Type	.570	1	.570	.525	.484
MWCO_Percent	115.630	5	23.126	21.300	.000
Error	11.943	11	1.086		
Total	5273.841	18			
Corrected Total	130.833	17			

R Squared = .909 (Adjusted R Squared = .859)

Table 4.60: Two way ANOVA resilient modulus

Source	Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	6123440.889 ^a	6	1020573.481	7.222	.003
Intercept	136400138.889	1	136400138.889	965.273	.000
Blends_Type	46368.444	1	46368.444	.328	.578
MWCO_Percent	6093835.333	5	1218767.067	8.625	.002
Error	1554380.222	11	141307.293		
Total	144077960.000	18			
Corrected Total	7677821.111	17			

a. R Squared = .798 (Adjusted R Squared = .687)

These findings underscore the important role of WCO content in enhancing both the stability and elastic properties of modified bitumen. The dependent variables, Marshall stability and resilient modulus, exhibit high R-squared values of 0.909 and 0.798, respectively, indicating that a substantial proportion of the variability in these performance metrics can be attributed to the concentration of WCO. Consequently, the

results suggest that the incorporation of WCO significantly improves the mechanical properties of bitumen, thereby enhancing its suitability for applications in road construction.

Table 4.61: Post hoc multiple comparisons of Marshall stability

(I) MWCO_Percent	(J) MWCO_Percent	Mean Difference (I- J)	Std. Error	Sig. ^b	95% Confidence Interval for Difference ^b	
					Lower Bound	Upper Bound
45:55_5%	45:55_10%	-5.287*	.851	.000	-7.159	-3.414
	45:55_15%	-.713	.851	.000	-2.586	1.159
	50:50_5%	-1.371	.868	.143	-3.282	.540
	50:50_10%	-7.004*	.868	.000	-8.915	-5.093
	50:50_15%	-1.888	.868	.052	-3.799	.024
45:55_10%	45:55_15%	4.573*	.851	.000	2.701	6.446
	50:50_5%	3.916*	.868	.001	2.005	5.827
	50:50_10%	-1.718	.868	.074	-3.629	.194
	50:50_15%	3.399*	.868	.002	1.488	5.310
45:55_15%	50:50_5%	-.658	.868	.465	-2.569	1.254
	50:50_10%	-6.291*	.868	.000	-8.202	-4.380
	50:50_15%	-1.174	.868	.203	-3.085	.737
50:50_5%	50:50_10%	-5.633*	.851	.000	-7.506	-3.761
	50:50_15%	-.517	.851	.556	-2.389	1.356
50:50_10%	50:50_15%	5.117*	.851	.000	3.244	6.989

*. The mean difference is significant at the .05 level.

Table 4.62: Post hoc multiple comparisons of resilient modulus

(I) MWCO_Percent	(J) MWCO_Percent	Mean Difference (I- J)	Std. Error	Sig. ^b	95% Confidence Interval for Difference ^b	
					Lower Bound	Upper Bound
45:55_5%	45:55_10%	633.000	306.928	.064	-42.544	1308.544
	45:55_15%	1338.333*	306.928	.001	662.789	2013.878
	50:50_5%	-144.556	313.257	.000	-834.030	544.919
	50:50_10%	523.444	313.257	.123	-166.030	1212.919
	50:50_15%	1353.444*	313.257	.001	663.970	2042.919
45:55_10%	45:55_15%	705.333*	306.928	.042	29.789	1380.878
	50:50_5%	-777.556*	313.257	.030	-1467.030	-88.081
	50:50_10%	-109.556	313.257	.000	-799.030	579.919
	50:50_15%	720.444*	313.257	.042	30.970	1409.919
45:55_15%	50:50_5%	-1482.889*	313.257	.001	-2172.363	-793.414
	50:50_10%	-814.889*	313.257	.025	-1504.363	-125.414
	50:50_15%	15.111	313.257	.962	-674.363	704.586
50:50_5%	50:50_10%	668.000	306.928	.052	-7.544	1343.544
	50:50_15%	1498.000*	306.928	.000	822.456	2173.544
50:50_10%	50:50_15%	830.000*	306.928	.021	154.456	1505.544

*. The mean difference is significant at the .05 level.

The post hoc multiple comparison results for Marshall stability and resilient modulus, presented in Table 4.61 and table 4.62, respectively, highlight the significant effects of WCO content on the mechanical properties of modified bitumen. In Table 4.61, the comparisons for Marshall stability reveal several significant differences. Notably, the mean difference between the 45:55 blend at 5% WCO and the 45:55 blend at 10% WCO is -5.287 ($p = 0.000$), indicating a significant increase in stability with higher WCO content. Similarly, the 50:50 blend at 10% WCO shows a mean difference of -7.004 ($p = 0.000$) compared to the 50:50 blend at 5% WCO, reinforcing the importance of WCO concentration in enhancing the stability of the bitumen blends. However, some comparisons, such as 45:55_5% vs. 50:50_5%, show non-significant differences (mean difference of -1.371, $p = 0.143$), suggesting that certain blends may not exhibit substantial differences in stability.

Table 4.62 represents the post hoc results for resilient modulus indicate significant mean difference between the 45:55 blend at 5% WCO and the 45:55 blend at 15% WCO is 1338.333 ($p = 0.001$), highlighting a substantial increase in modulus with higher WCO content. Additionally, the resilient modulus for the 50:50 blend at 15% WCO compared to the 50:50 blend at 5% WCO shows a mean difference of 1498.000 ($p = 0.000$), further underscoring the impact of WCO on enhancing the elastic properties of the modified bitumen. Notably, comparisons involving the 50:50 blends exhibit significant differences, particularly between 50:50_5% and 50:50_10%, with a mean difference of 668.000 ($p = 0.052$), suggesting potential improvements in modulus as WCO content increases. Figure 4.67 and Figure 4.68 depicts marginal means and highlights the significant variation on independent variables MWCO_Percent. As expected, the resilient modulus has followed the downward trend compared to lower percent of the WCO in the modification of the asphalt mixtures.

The results collectively suggest that optimizing WCO content in bitumen formulations can lead to enhanced durability and resistance to deformation under traffic loads.

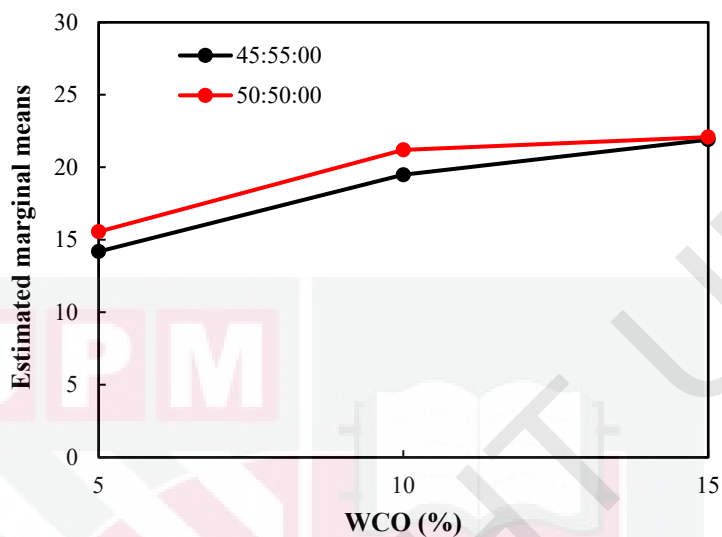


Figure 4.67: Estimated means of Marshall stability at varying WCO%

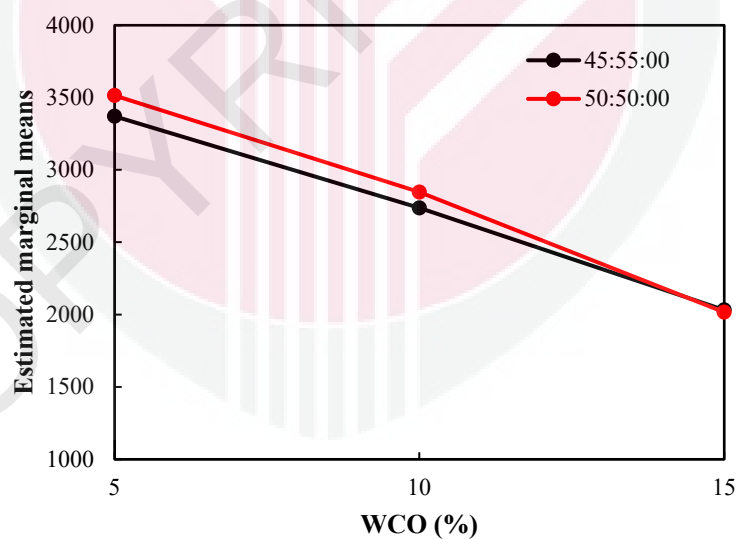


Figure 4.68: Estimated means of resilient modulus at varying WCO%

4.16 Summary

The effect of the WCO on the properties of the bitumen and the asphalt mixture is evaluated in this study. However, prior to the utilization of the WCO into the bitumen for modification, the pre-processing and modification of the raw WCO were followed to reduce the deficiencies encountered previously in the performance of the bitumen. Initially, the WCO was modified to change its structure from liquid to rubbery solid at various SBS:WCO ratios and the promising ratio was selected best on the initial trial and error method. The preliminary raw material characteristics were assessed, and the result suggested that all are within the required specifications. Secondly, the modified waste cooking oil granulates (MWCOG) with ratios of 45:55 and 50:50 was incorporated into bitumen to evaluate the unaged and aged rheological, chemical and morphological properties. It is revealed that both ratios, i.e., MWCOG-45:55 and MWCOG-50:50 had performed better than the base bitumen. However, the higher content of the MWCOG has significantly caused a reduction in the performance of the modified bitumen. Therefore, the incorporation of the MWCOG up to 15% in both cases has promising performance. The optimum bitumen content of selected bitumen blends was determined and the increasing content of the MWCOG for the bitumen modification eventually decreased the OBC of the asphalt mixtures. Lastly, the mechanical performance of the modified asphalt mixtures was evaluated, and it was revealed that the MWCOG-5% and MWCOG-10% modified asphalt mixtures have shown promising performance for both ratios in terms of stiffness, rutting and adhesion properties.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Introduction

The study intends to investigate the effect of modified waste cooking oil on the bitumen and asphalt mixture performance properties. The modified waste cooking oil (MWCOG-45:55 and MWCOG-50:50) was added to the base bitumen at 5%, 10%, 15%, 20% and 25%. The modified bitumen blends underwent comprehensive characterization encompassing rheological, physical, morphological and chemical properties. Following the process of elimination, seven promising performing modified bitumen blends have opted for the asphalt mixture characterisation. The selected asphalt mixture was tested and analysed for stiffness properties, rutting, stability and adhesion properties. Based on the study outcomes from the thesis, the main findings are rendered and concluded below.

5.2 Conclusion

The characterization of the raw materials i.e., bitumen, WCO, and aggregates was followed in the study's first objective. Additionally, particular emphasis was placed on the pre-modification of the WCO to mitigate the deficiencies and limitations encountered in its raw form. The preliminary raw materials assessment suggests that the results are within the specification and suitable for the subsequent analysis. Nevertheless, the filtered WCO was modified by blending the SBS: WCO at 20:80,

30:70, 40:60, 45:55 and 50:50. The modified WCO granulates (MWCOG) were blended with bitumen at various ratios with concentrations of 5%, 10%, 15%, 20%, and 25% by weight. These blended modified bitumens underwent testing for rotational viscosity and rutting parameters at different temperatures. Each tested bitumen underwent a comprehensive analysis to assess its suitability for further evaluation. Hence, the key finding is that the optimum ratio suitability for the bitumen modification is MWCOG-45:55 and MWCOG-50:50. Furthermore, microscale morphologies analysis of MWCOG showed that the waste cooking oil with SBS has produced a rubbery solid material with clear physical homogeneity and non-presence of the SBS.

The second objective of the study was to evaluate the effectiveness of the MWCOG-45:55 and MWCOG-50:50 on bitumen's rheological, physical, morphological and chemical properties. Based on the viscosity results, the increasing content of the MWCOG has increased the stiffening and improved the temperature susceptibility of the base bitumen. Adding 5–25 wt.% of MWCOG-45:55 improves the viscosities in the range of 513–3512.2 cp at 135 °C. However, the MWCOG-50:50 displayed a slightly higher viscosity in the same range with values of 562.1–2988.2 cp. However, the modified bitumen 45:55-25 and 50:50-25 are undesirable owing to higher viscosities beyond the SHRP specifications. The isochrones of the modified bitumens indicated the enhancement in G^* on increasing the concentration of MWCOG and as expected the δ decreases showing the elastic behaviour of bitumens. It is noteworthy that the performance grading of the base bitumen is improved from 64 °C to 76 °C whilst adding the 10% of MWCOG-50:50. The MWCOG-45:55 has demonstrated a maximum of PG76 however the MWCOG-50:50 has achieved the PG82 even at a 20%

incorporation of MWCOG. Moreover, the Black space diagram curves have shifted towards the lower δ with smooth curves indicating the improvement in the performance of the modified bitumens, and 45:55-25 and 50:50-25 curves are not desirable, indicating the marginal change in δ at higher and lower temperatures. Furthermore, the master curve of modified bitumens with MWCOG demonstrated an improved viscoelastic response at lower frequencies. The master curve of 45:55-15 has higher stiffness at a lower frequency than other bitumen curves and is less stiff at a higher frequency. The storage stability test explicated that the separation indices (SIs) based on the complex modulus at a temperature of 64 °C of the modified bitumen are within the specified range regardless of the 45:55-25% and 50:50-25%. Furthermore, the addition of MWCOG-45:55 and MWCOG-50:50 into base bitumen by 10wt% demonstrated no significant change in the spectra of 45:55-10% and 50:50-10%. However, the absorptions of peaks at a range of 1850 cm^{-1} –1650 cm^{-1} are more intense than the peak of the base bitumen. A similar peak has been identified in the WCO, MWCOG-45:55, and MWCOG-50:50 spectra which corresponds to the dominance of the ester and the ketones at 1743 cm^{-1} . The modified blends 45:55-10 and 50:50-10% were selected to be exploited as standard to identify any changes in the microstructure of modified blends. It was observed that there is no such difference between 45:55-10% and 50:50-10% which further clarifies the principle of the rapid dissolvment of SBS particles in WCO. However, the observed SBS particles in the MWCOG-45:55 and MWCOG-50:50 have fully dissolved within the bitumen matrix. In a nutshell, the modified bitumen 45:55-15% and 50:50-10% have shown optimal rheological performance.

The third objective's findings for the selective Marshall mix design are derived from the process of elimination established in the second objective, which assesses the OBC. The results suggested that the increasing content of the MWCOG for the bitumen modification eventually decreases the OBC of the asphalt mixtures. The variance in the OBC among the asphalt mixtures is minimal in comparison to the control mixture. The control mixture OBC is 5.04% which is higher than 45:55-10% and 50:50-10% with 4.92% and 4.89% respectively. However, the MWCOG-45:55 exhibits a relatively lower OBC with higher MWCOG content when compared to MWCOG-50:50. This lower OBC can be attributed to the reduced stiffness of the bitumen following modification, distinct from MWCOG-50:50. Furthermore, the increased presence of WCO within the composite material contributes to enhanced smoothness during the mixing of the mixture. On the other hand, 50:50-15% has shown an OBC of 4.93% which is higher than the other modified bitumens. The increased OBC corresponds to the enhancement in the viscosity of the bitumens which ultimately requires more bitumen content to uniformly coat the asphalt mixture. The OBC was then employed for the mechanical analysis of the asphalt mixtures.

The study's fourth objective involved evaluating the mechanical characteristics of the opted asphalt mixtures, focusing on the resilient modulus, permanent deformation and adhesion properties. It can be observed from the outcomes that there is no notable enhancement in the overall stiffness of asphalt mixtures on the incorporation of the MWOCGs. However, the 45:55-5% and 50:50-5% have demonstrated an improvement of 13.5% and 0.33% respectively. It is revealed that MWCOG-45:55 have an overall minimum resilient modulus compared to that of the MWCOG-50:50. The resilient modulus of >2500 Mpa is desirable for the AC14 asphalt mixtures

following the specification of the JKR and the 45:55-15% and 50:50-15% have not satisfied the minimum criterion. Additionally, the permanent deformation evaluation showed that the incorporation of MWCOG significantly decreased the cumulative strain of modified asphalt mixtures. The 45:55-5% and 45:55-10% have a strain value of 0.46% and 0.54% which is lower than the 0.63% of the control mixtures. Similarly, the 50:50-5% and 50:50-10% reduced the strain to 0.54% and 0.62%. However, the control mixture has demonstrated a lower creep modulus of 239 Mpa which is lower than the creep modulus of 45:55-5% and 45:55-10% with values of 323 Mpa and 277 Mpa respectively. Similarly, the 50:50-5% and 50:50-10% MWCOG modified asphalt mixtures have displayed 278 Mpa and 241 Mpa respectively. Hence, all modified mixtures have satisfied the minimum requirement of the creep modulus (≥ 75 Mpa). Whereas, the creep rate of the asphalt mixtures exhibits an inverse relationship with the creep modulus. The 45:55-5% and 45:55-10% modified asphalt mixture has displayed an improvement of 27% and 24% with creep rate values of 0.00021 and 0.00022 in comparison to the control mixture (0.00029) respectively. The 50:50-5% and 50:50-10% achieved 0.00025 and 0.00023 with 13% and 20% improvement compared to the control mixture. The durability, resistance to disintegration and cohesion loss of the asphalt mixture is assessed through the Cantabro test. The average loss of the control specimens is 2.50% which is higher among all the modified mixtures. However, the MWCOG-45:55 demonstrated an overall lower average loss compared to the MWCOG-50:50. The 45:55-15% and 50:50-15% have shown a 61% and 50% improvement in comparison to that of the control mixture. Thus, the study outcomes suggested that the modified WCO incorporation of up to 10% has a significant impact on the properties of the bitumen and modified asphalt mixtures and possibly be an economical and sustainable modifier in pavement constructions.

In light of these findings, this research addressed a significant gap in the sustainable modification of bitumen through a novel technique that transforms waste cooking oil (WCO) into a semi-solid structure for dry modification with styrene-butadiene-styrene (SBS). Enhancements in the homogeneity and performance of the modified bitumen make WCO a viable eco-friendly alternative. Additionally, this approach mitigates common challenges associated with using SBS alone, such as high-temperature processing and prolonged mixing times. This contribution not only promotes recycling efforts and reduces environmental impact but also provides key insights for utilizing WCO efficiently, leading to more sustainable pavement solutions.

5.3 Recommendations for further research

The study concludes by highlighting possible avenues for future research. The findings underscore several key areas that require further attention to improve the understanding of WCO-modified bitumen.

1. In this study, the raw waste cooking oil underwent a simple filtration process to transition from an oily state to a rubbery solid state. However, it's advisable to consider additional pre-purification or chemical treatments like transesterification after the filtration. These steps can further enhance the properties of the waste cooking oil and provide deeper insights into the behaviours of the modified bitumen. Additionally, conducting a comparative analysis might improve the overall applicability of the modified bitumen.
2. Performing the Life cycle assessment of the WCO as a bitumen modifier is an important step to evaluate the environmental impact across the production and its application. This assessment is likely to quantify the WCO-modified bitumen potential in lowering the impact on the environment compared to the original bitumen.
3. The bitumen's higher and intermediate temperature rheological properties were mainly focused in this research. Whereas lower temperature performance of the modified bitumen is desirable to fully understand the behaviour. While the study concentrates on tropical regions characterized by temperatures ranging from 22 °C to 32 °C, the broader applicability of modified WCO granulates as

a bitumen modifier necessitates consideration across various aspects. Specifically, the evaluation should encompass low-temperature properties, which typically measure fatigue resistance and susceptibility to cracking.

4. The OBC of the asphalt mixture were determined by employing the Marshall mix design. Nevertheless, the more advanced method i.e., the Superpave mix design is highly recommended to evaluate the more detailed performance and to compare results with the Marshall mix design. The Superpave design method followed the gyratory compactor which simulated more the field conditions. This method usually reflects the climate, traffic and integral properties of the materials to design an optimised asphalt mixture and pavement with long-term service life.



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APPENDICES

Appendix A

Table A1: Rotational viscosity results of modified bitumen at 30:70

Blend type	Viscosity (cp)			
	90 °C	110 °C	135 °C	165 °C
Base	5770.5	1556.8	429	138.6
30:70-5%	5770.2	1557.6	428.5	138.8
30:70-10%	7188.0	1354.7	395.7	119.1
30:70-15%	6190.6	1578.3	405.9	139.9
30:70-20%	7216.4	1829.3	544.9	171.4
30:70-25%	7753.4	2544.8	685.9	219.7

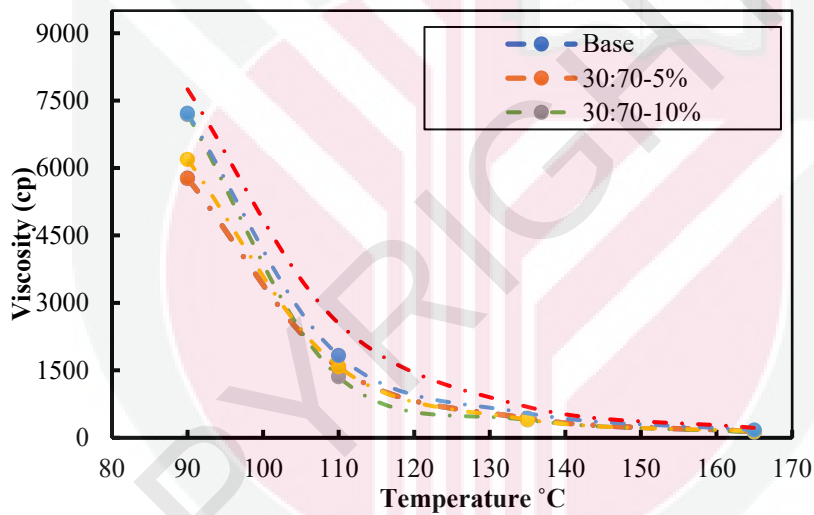


Figure A1: Viscosity results of 30:70 modified bitumen at varying temperatures

Table A2: Mixing and compaction temperatures of 30:70 modified blends

Blend type	Viscosity (Pa.s)		Mixing temperature °C	Compaction temperature °C
	135 °C	165 °C		
Base	0.430	0.138	160	145
30:70-5%	0.395	0.119	156	143
30:70-10%	0.439	0.140	160	147
30:70-15%	0.545	0.170	165	153
30:70-20%	0.686	0.220	170	158
30:70-25%	0.702	0.210	172	158

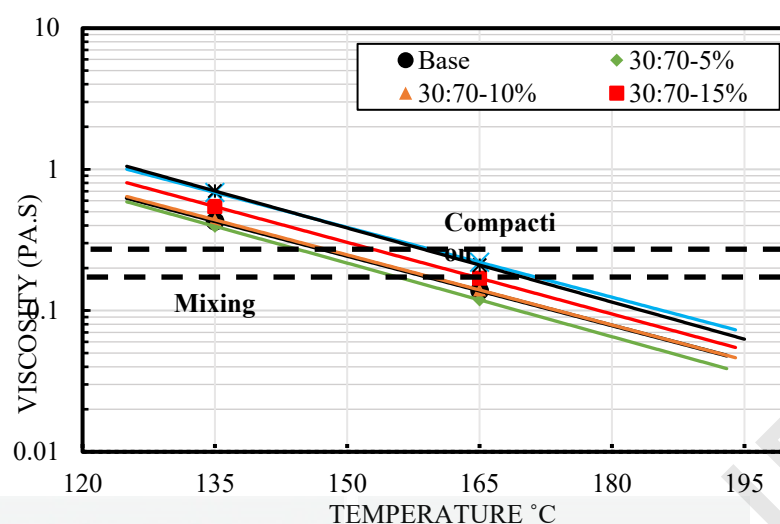


Figure A2: Viscosity-temperature relationship of 30:70 blends

Table A3: Rutting parameter of 30:70 at varying temperatures

Blend type	Rutting parameter (kPa)					
	52°C	58°C	64°C	70°C	76°C	82°C
Base	7.07	3.16	1.43	0.65	0.33	0.23
30:70-5%	5.80	2.41	1.20	0.72	0.42	0.42
30:70-10%	6.90	2.90	1.83	0.82	0.64	0.46
30:70-15%	5.87	1.90	1.74	1.03	0.99	0.50
30:70-20%	6.03	2.45	2.44	1.38	1.07	0.57
30:70-25%	7.04	3.00	3.73	2.15	1.79	0.66

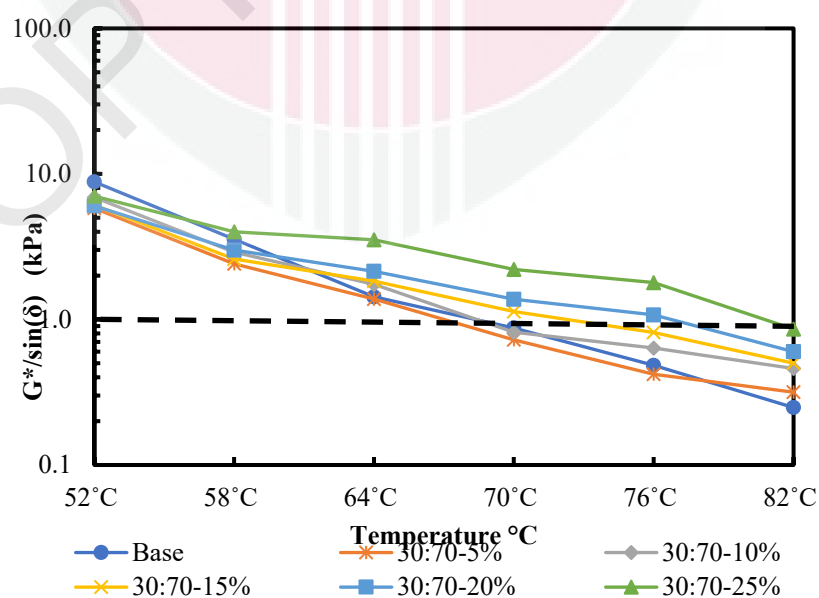


Figure A3: Temperature effect on rutting parameter of 30:70 modified blends

Table A4: Rotational viscosity results of modified bitumen at 40:60

Blend type	Viscosity (cp)			
	90 °C	110 °C	135 °C	165 °C
Base	5770.2	1557.6	428.5	138.8
40-60-5%	7949.1	2183.3	492.9	164.1
40-60-10%	-	2315.6	662.2	213.3
40-60-15%	-	2948.2	923.9	285.0
40-60-20%	-	3499.9	1160.1	444.6
40-60-25%	-	5216.7	1507.5	544.7

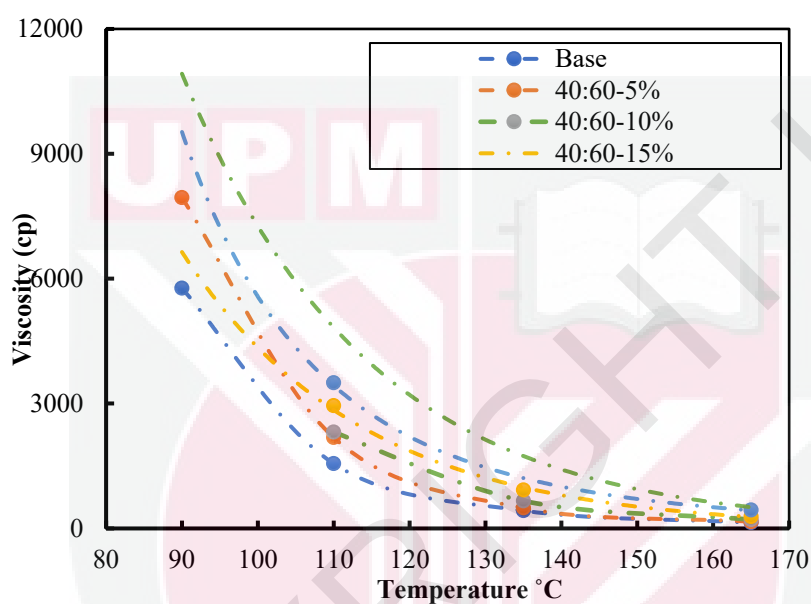


Figure A4: Viscosity results of 40:60 modified bitumen at varying temperatures

Table A5: Mixing and compaction temperatures of 40:60 modified blends

Blend type	Viscosity (Pa.s)		Mixing temperature °C	Compaction temperature °C
	135 °C	165 °C		
Base	0.430	0.138	160	145
40-60-5%	0.493	0.164	165	150
40-60-10%	0.662	0.213	171	159
40-60-15%	0.924	0.285	179	165
40-60-20%	1.160	0.445	195	181
40-60-25%	1.508	0.545	>200	185

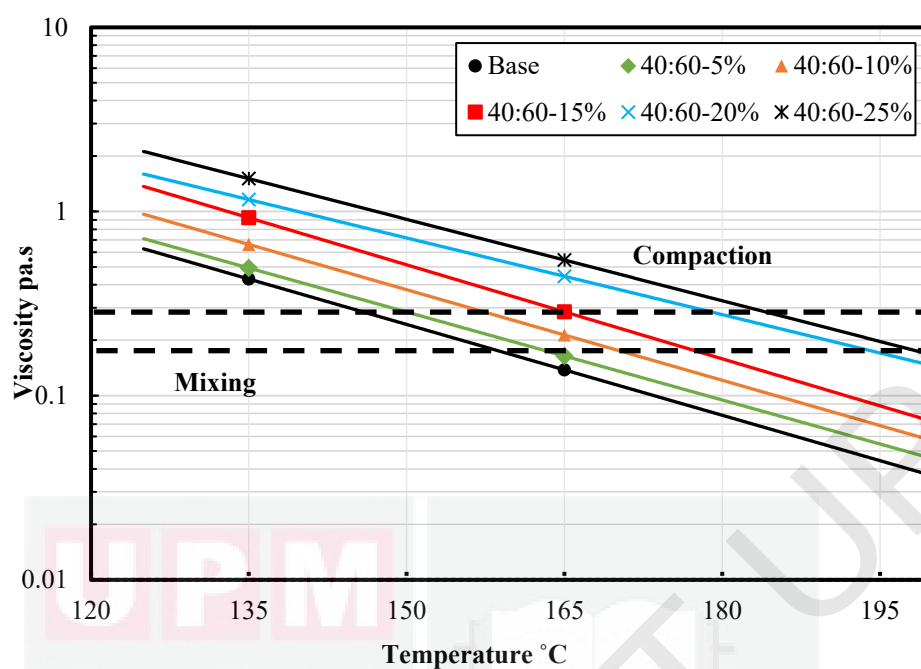


Figure A5:Viscosity-temperature relationship of 40:60 blends

Table A6: Rutting parameter of 40:60 at varying temperatures

Blend type	Rutting parameter (kPa)					
	52°C	58°C	64°C	70°C	76°C	82°C
Base	7.07	3.16	1.43	0.65	0.33	0.23
40-60-5%	6.64	3.19	1.29	0.75	0.42	0.27
40-60-10%	9.23	4.48	2.25	1.16	0.64	0.36
40-60-15%	8.36	4.75	2.43	1.52	0.99	0.50
40-60-20%	8.94	5.45	3.19	2.08	1.07	0.65
40-60-25%	11.07	7.40	4.98	3.41	1.79	0.90

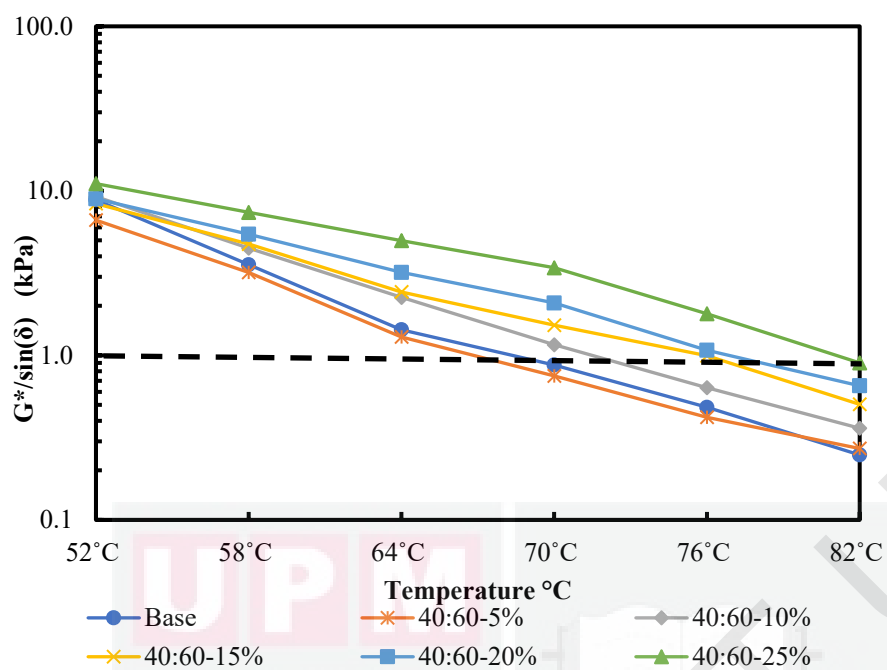


Figure A6: Temperature effect on rutting parameter of 40:60 modified blends

Table A7: Rotational viscosity results of modified bitumen at 45:55

Blend type	Viscosity (cp)			
	90 °C	110 °C	135 °C	165 °C
Base	5770.2	1557.6	428.5	138.8
45:55-5%	8211.8	2197.3	513.3	150.0
45:55-10%	-	3140.8	806.3	237.3
45:55-15%	-	2735.0	1350.0	406.0
45:55-20%	-	-	1987.5	550.2
45:55-25%	-	-	3512.2	1292.3

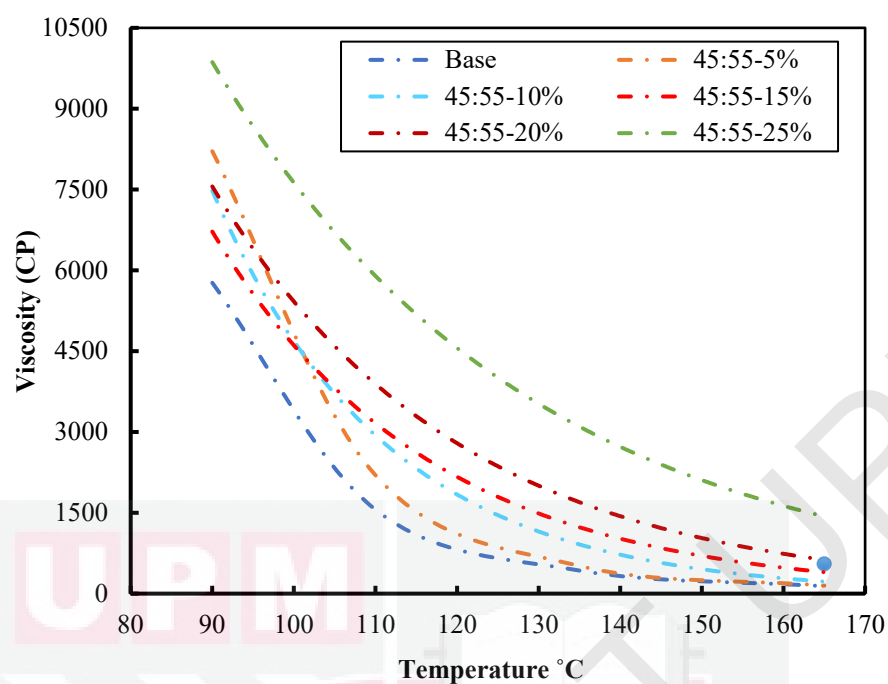


Figure A7: Viscosity results of 45:55 modified bitumen at varying temperatures

Table A8: Mixing and compaction temperatures of 45:55 modified blends

Blend type	Viscosity (Pa.s)		Mixing temperature °C	Compaction temperature °C
	135 °C	165 °C		
Base	0.430	0.138	160	145
45:55-5%	0.513	0.150	163	150
45:55-10%	0.806	0.238	173	163
45:55-15%	1.350	0.406	181	174
45:55-20%	1.987	0.550	191	182
45:55-25%	2.712	0.894	>200	195

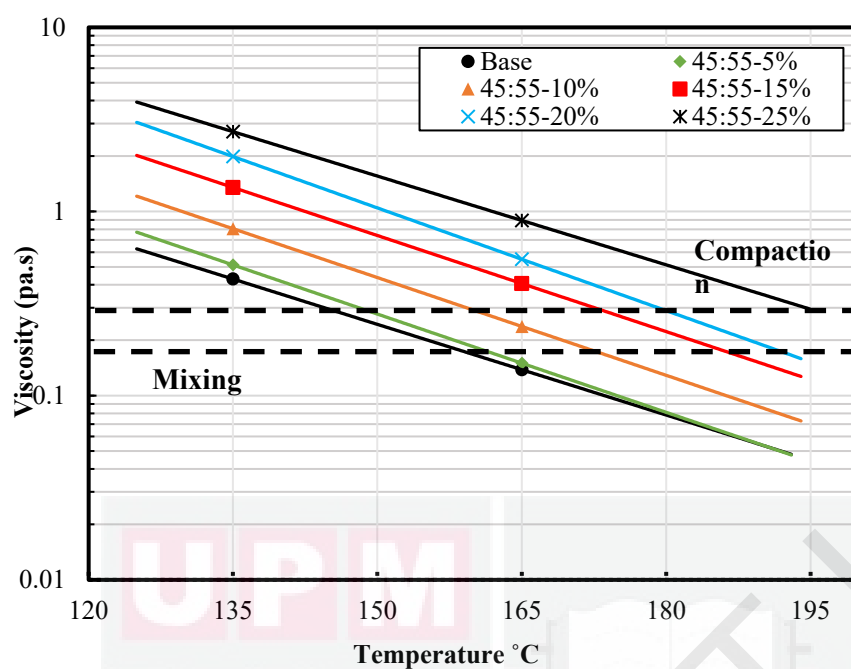


Figure A8:Viscosity-temperature relationship of 45:55 blends

Table A9:Rutting parameter of 45:55 at varying temperatures

Blend type	Rutting parameter (kPa)					
	52°C	58°C	64°C	70°C	76°C	82°C
Base	7.07	3.16	1.43	0.65	0.33	0.23
45:55-5%	8.05	3.56	1.61	0.82	0.52	0.30
45:55-10%	10.59	4.49	2.35	1.27	0.71	0.44
45:55-15%	10.68	4.71	2.44	1.52	0.98	0.50
45:55-20%	12.77	5.45	3.21	2.05	1.16	0.62
45:55-25%	25.42	11.69	5.43	3.09	1.71	0.79

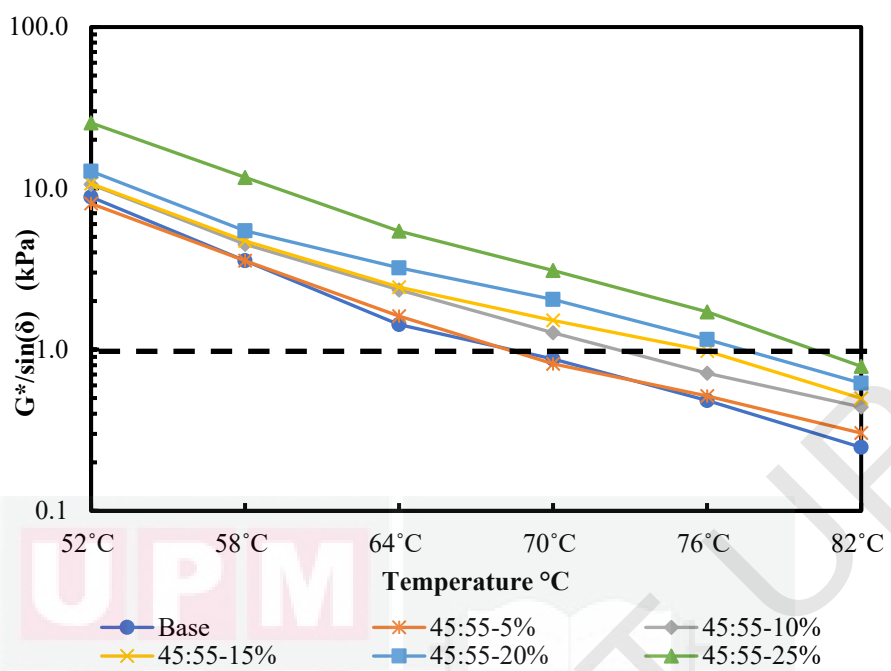


Figure A9: Temperature effect on rutting parameter of 45:55 modified blends

Appendix B

Table B 1: Volumetric properties of 45:55-5% mixture

Sample No	% AC	Sample height (mm)	Weight (g)			Specific gravity			Voids (%)			Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA						
4.0-I	4.0	63.5	1182.4	674.3	1188.1	2.301	2.458	6.37	15.45	58.78		1	13.43	13.43	4.94	3962
4.0-II	4.0	63.4	1184.6	677.3	1194.8	2.289	2.458	6.87	15.90	56.82		1	14.94	14.94	3.69	4765
4.0-III	4.0	64.3	1182	678.1	1189.6	2.311	2.458	5.98	15.10	60.40		0.98	18.23	17.87	3.8	4632
Average		63.72	1183	676.6	1190.8	2.300	2.458	6.40	15.48	58.67		0.99	15.53	15.41	4.14	4453
4.5-I	4.5	63.37	1190.1	681.9	1194.3	2.323	2.440	4.81	15.11	68.15		1	15.43	15.43	4.16	4378
4.5-II	4.5	64.07	1191.1	683.4	1197.3	2.318	2.440	5.01	15.29	67.23		0.98	15.16	14.86	4.47	3305
4.5-III	4.5	63.67	1194.5	680.7	1199.3	2.303	2.440	5.60	15.82	64.58		0.99	20.08	19.88	4.26	4199
Average		63.7	1191.9	682.0	1197.0	2.315	2.440	5.143	15.41	66.65		0.99	16.89	16.72	4.30	3961
5.0-I	5.0	64.03	1202.3	692.4	1204.2	2.349	2.423	3.03	14.59	79.25		0.98	16.34	16.01	4.03	4648
5.0-II	5.0	63.63	1200.5	690.1	1206.1	2.327	2.423	3.96	15.41	74.30		0.99	15.64	15.48	4.48	4793
5.0-III	5.0	63.7	1197.4	687.5	1203.5	2.321	2.423	4.21	15.63	73.07		0.99	13.52	13.38	4.33	3909
Average		63.8	1200.1	690.0	1204.6	2.332	2.423	3.733	15.21	75.54		0.99	15.99	15.75	4.28	4450
5.5-I	5.5	64.07	1205.4	695.7	1209.7	2.345	2.405	2.50	15.19	83.55		0.98	14.55	14.26	5.46	3683
5.5-II	5.5	63.8	1203.7	692.8	1208.1	2.336	2.405	2.88	15.52	81.43		0.99	15.09	14.94	5.54	2856
5.5-III	5.5	63.57	1198.2	686.6	1201.4	2.328	2.405	3.23	15.82	79.58		0.99	14.08	13.94	4.79	3689
Average		63.8	1202.4	691.7	1206.4	2.336	2.405	2.87	15.51	81.52		0.99	14.57	14.38	5.26	3409.3
6.0-I	6.0	63.77	1203.8	692.9	1205.9	2.347	2.388	1.74	15.58	88.82		0.99	14.89	14.74	6.04	3346
6.0-II	6.0	63.51	1201.5	690.9	1204.7	2.338	2.388	2.08	15.88	86.88		0.99	14.62	14.47	5.67	3289
6.0-III	6.0	64.33	1204.5	695.1	1208.4	2.347	2.388	1.74	15.58	88.82		1	12.21	12.21	7.29	3056
Average		63.9	1203.3	692.97	1206.3	2.344	2.388	1.856	15.68	88.17		0.99	13.91	13.81	6.33	3230

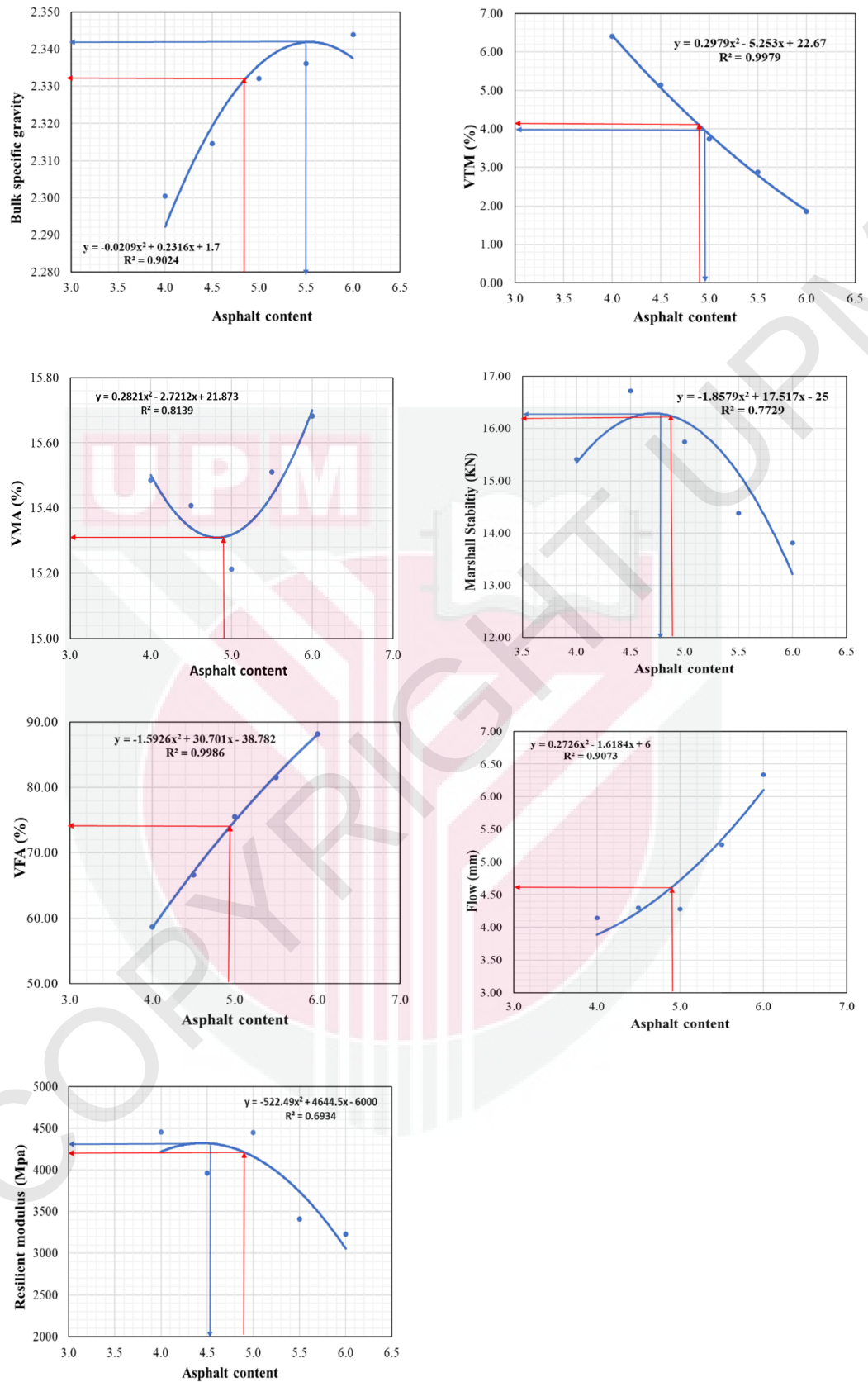


Figure B1: Optimum bitumen content determination plots for 45:55-5%

Table B2: Marshall mix design results of 45:55-5%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.9025	-
Bulk density	2.333	-
Stability (KN)	16.22	>8KN
VTM (%)	4.077	3-5%
VMA (%)	15.31	>15%
Resilient Modulus (Mpa)	4211.8	>2500
Flow (mm)	4.61	2.0-4.0 (mm)
VFA (%)	74.45	70-80%



Table B3: Volumetric properties of 45:55-10% mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)			Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA					
4.0-I	4.0	64.7	1182.1	675.1	1190.4	2.294	2.457	6.62	15.72	57.91	0.97	18.37	17.82	4.57	3236
4.0-II	4.0	64.5	1184.5	672.6	1189.8	2.290	2.457	6.77	15.86	57.31	0.97	16.22	15.73	3.99	3358
4.0-III	4.0	64.2	1179.1	671.7	1184.8	2.298	2.457	6.45	15.57	58.56	0.98	16.52	16.19	3.98	3653
	Average	64.5	1181.9	673.1	1188.3	2.294	2.457	6.61	15.72	57.93	0.973	17.04	16.58	4.18	3415.7
4.5-I	4.5	63.77	1190.4	687.2	1198.9	2.326	2.439	4.60	14.98	69.27	0.99	17.89	17.71	3.16	3798
4.5-II	4.5	64.17	1191.8	683.5	1199.5	2.310	2.439	5.29	15.59	66.08	0.98	16.74	16.41	4.44	3392
4.5-III	4.5	63.7	1187.9	684.1	1195.3	2.324	2.439	4.71	15.07	68.75	0.99	19.52	19.32	4.01	3651
	Average	63.9	1190.0	684.9	1197.9	2.320	2.439	4.866	15.21	68.03	0.99	18.05	17.81	3.87	3614
5.0-I	5.0	64	1194	688.7	1198.3	2.343	2.421	3.22	14.82	78.27	0.98	18.66	18.29	4.81	2681
5.0-II	5.0	64.2	1195.3	691	1203.6	2.332	2.421	3.68	15.22	75.82	0.98	17.98	17.62	4.22	3598
5.0-III	5.0	63.6	1191.5	685.5	1196.3	2.333	2.421	3.65	15.19	75.99	0.99	16.83	16.66	4.61	3101
	Average	63.9	1193.6	688.4	1199.4	2.336	2.421	3.52	15.08	76.69	0.98	17.82	17.52	4.55	3127
5.5-I	5.5	63.47	1205.1	697.3	1208.3	2.358	2.404	1.88	14.71	87.21	1.00	16.58	16.58	4.96	3004
5.5-II	5.5	63.87	1201.2	695.1	1205.2	2.355	2.404	2.03	14.84	86.34	0.99	15.88	15.72	4.23	3114
5.5-III	5.5	63.73	1205.3	692.6	1210.9	2.325	2.404	3.25	15.90	79.58	0.99	16.92	16.75	5.52	3469
	Average	63.7	1203.9	695.0	1208.1	2.346	2.404	2.38	15.15	84.38	0.99	16.46	16.35	4.90	3195.7
6.0-I	6.0	63.6	1203.3	692.3	1206.4	2.341	2.386	1.92	15.80	87.86	0.99	12.39	12.27	4.38	2161
6.0-II	6.0	63.9	1202.2	693.6	1203.7	2.357	2.386	1.24	15.22	91.85	0.99	12.43	12.31	6.45	1811
6.0-III	6.0	63.5	1202.6	694.5	1204.8	2.357	2.386	1.25	15.22	91.82	1	13.81	13.81	6.89	2390
	Average	63.7	1202.7	693.5	1205.0	2.351	2.386	1.47	15.41	90.51	0.99	12.88	12.79	5.91	2121

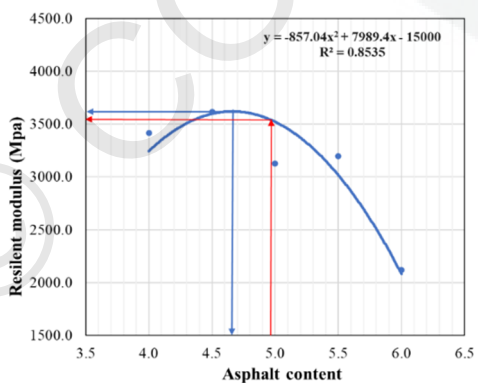
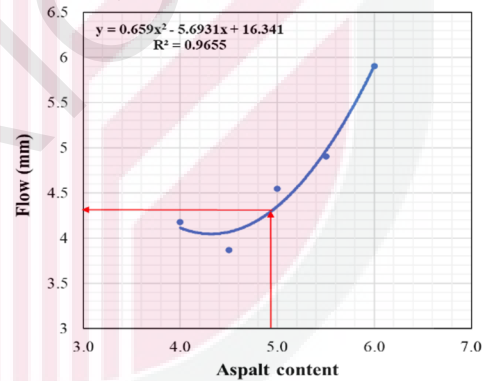
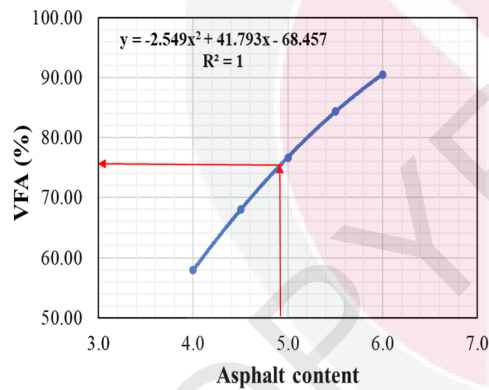
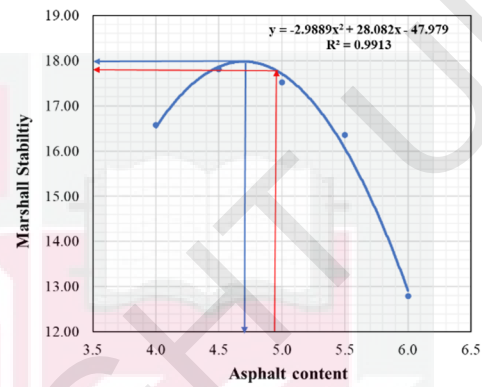
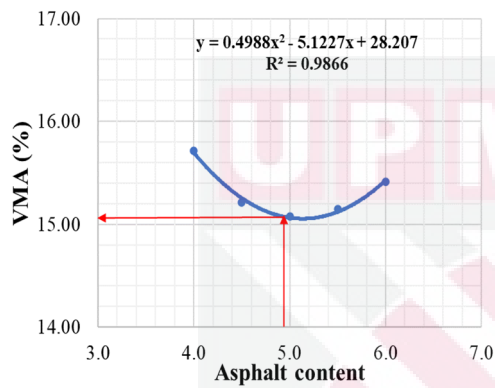
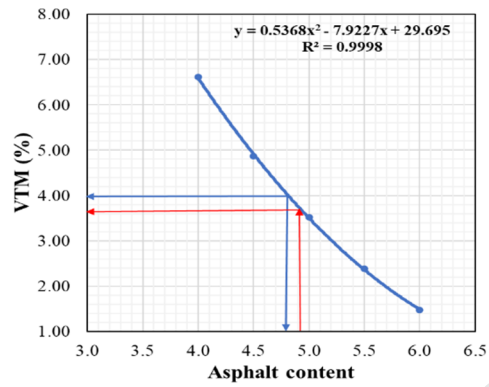
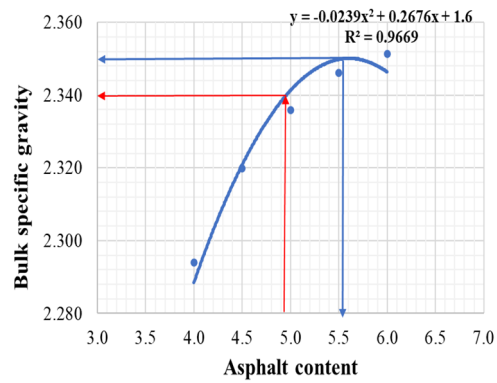


Figure B2: Optimum bitumen content determination plots for 45:55-10%

Table B4: Marshall mix design results of 45:55-10%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.922	-
Bulk density	2.338	-
Stability (KN)	17.83	>8KN
VTM (%)	3.702	3-5%
VMA (%)	15.07	>15%
Resilient Modulus (Mpa)	3558.9	>2500
Flow (mm)	4.284	2.0-4.0 (mm)
VFA (%)	75.5	70-80%



Table B5: Volumetric properties of 45:55-15% mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)			Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA					
4.0-I	4.0	64.7	1176.2	671.8	1182.8	2.302	2.455	6.25	15.43	59.49	0.97	16.97	16.46	4.39	2640
4.0-II	4.0	64.0	1183.6	674.9	1192.8	2.285	2.455	6.92	16.04	56.85	0.98	15.85	15.53	4.12	2470
4.0-III	4.0	65.0	1182.6	672.1	1190.6	2.281	2.455	7.11	16.20	56.15	0.96	15.37	14.76	4.34	2913
Average		64.57	1180.8	672.93	1188.7	2.289	2.455	6.76	15.89	57.50	0.97	16.06	15.58	4.28	2555
4.5-I	4.5	63.9	1190.6	685.2	1197.1	2.326	2.437	4.57	14.99	69.53	0.99	16.81	16.64	4.6	2586
4.5-II	4.5	65.47	1189.5	673.2	1189.2	2.305	2.437	5.42	15.75	65.61	0.95	17.67	16.79	5.07	2505
4.5-III	4.5	64.4	1185	678.5	1189.6	2.319	2.437	4.87	15.26	68.09	0.97	15.42	14.96	5.33	2250
Average		64.6	1188.4	679.0	1192.0	2.317	2.437	4.95	15.34	67.75	0.97	11.49	16.13	5.00	2447
5.0-I	5.0	64.17	1188	688.3	1194.7	2.346	2.419	3.04	14.71	79.36	0.98	16.77	16.43	4.35	2264
5.0-II	5.0	63.7	1188.1	686.4	1196.6	2.329	2.419	3.75	15.34	75.55	0.99	16.67	16.50	4	2590
5.0-III	5.0	63.6	1190.4	689.3	1199.7	2.332	2.419	3.60	15.21	76.32	0.99	16.95	16.78	5.34	2286
Average		63.8	1188.8	688.0	1197.0	2.336	2.419	3.46	15.08	77.077	0.99	16.80	16.57	4.56	2380
5.5-I	5.5	63.83	1197.1	692.2	1199.5	2.360	2.402	1.75	14.66	88.04	0.99	15.73	15.57	5.77	1839
5.5-II	5.5	64	1211.3	701.4	1215.6	2.356	2.402	1.92	14.81	87.02	0.98	16.18	15.86	5.74	2008
5.5-III	5.5	64.07	1215.7	700.1	1218.2	2.346	2.402	2.31	15.14	84.76	0.98	13.38	13.11	5.17	1709
Average		64.0	1208.0	697.9	1211.1	2.354	2.402	1.99	14.87	86.60	0.98	15.10	14.85	5.56	1852.0
6.0-I	6.0	64.3	1204.8	694.5	1206.8	2.352	2.385	1.38	15.40	91.06	0.98	14.31	14.02	6.98	1707
6.0-II	6.0	64.2	1213.4	701.8	1216.7	2.357	2.385	1.17	15.22	92.28	0.98	15.4	15.09	5.93	1940
6.0-III	6.0	63.8	1218.9	700.8	1220.1	2.347	2.385	1.57	15.56	89.92	0.99	13.85	13.71	5.99	2220
Average		64.1	1212.4	699.03	1214.533	2.352	2.385	1.37	15.39	91.09	0.98	14.52	14.28	6.30	1824

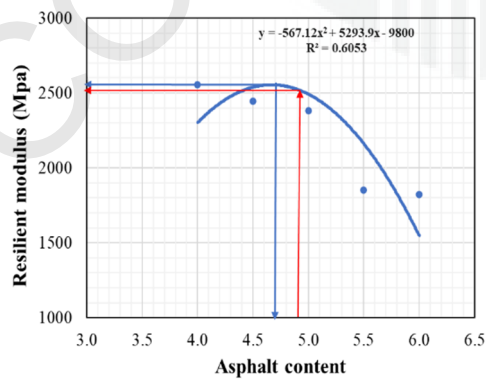
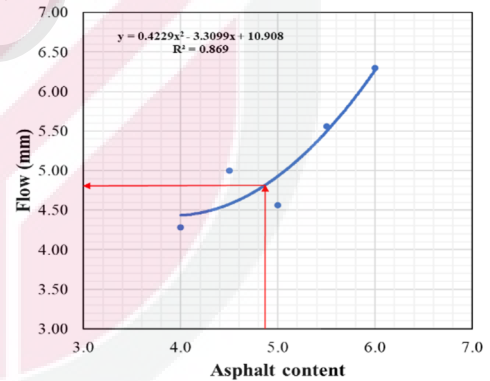
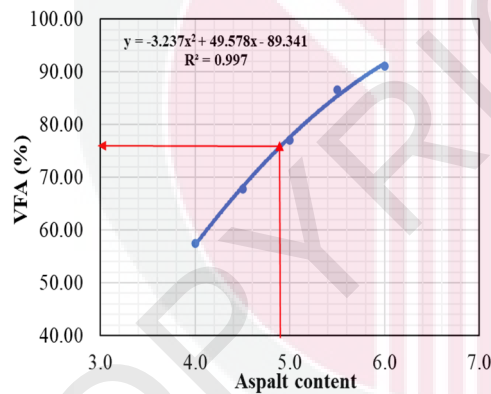
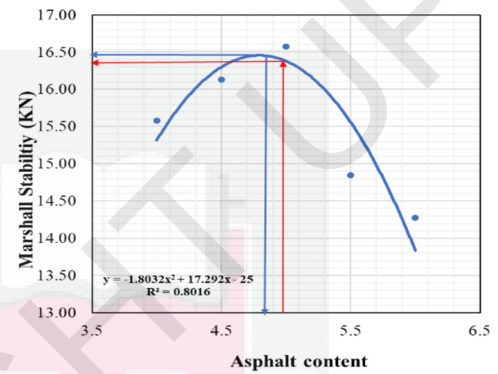
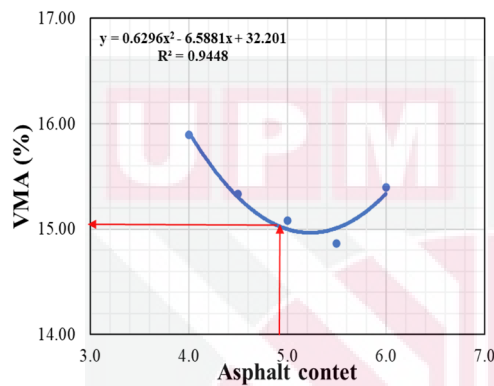
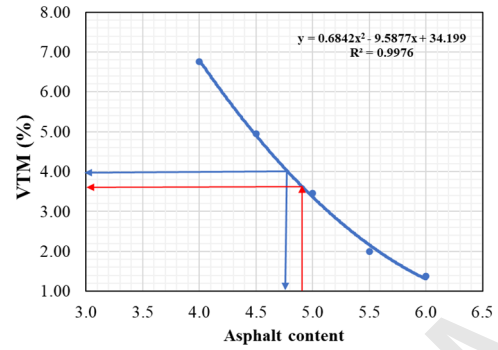
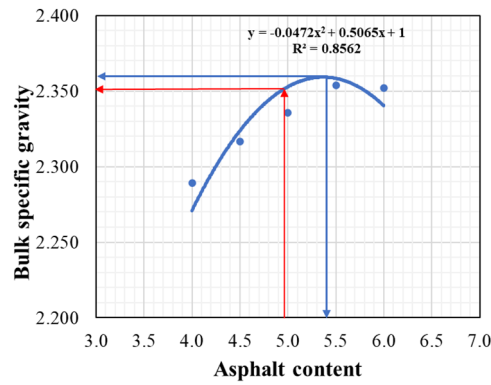


Figure B3: Optimum bitumen content determination plots for 45:55-15%

Table B6: Marshall mix design results of 45:55-15%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.91	-
Bulk density	2.349	-
Stability (KN)	16.43	>8KN
VTM (%)	3.609	3-5%
VMA (%)	15.03	>15%
Resilient Modulus (Mpa)	2520.86	>2500
Flow (mm)	4.851	2.0-4.0 (mm)
VFA (%)	76.21	70-80%



Table B7: Volumetric properties of 50:50-5% mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)			Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA					
4.0-I	4.0	63.7	1176.3	671.5	1183.1	2.299	2.458	6.45	15.53	58.46	0.99	17.71	17.53	3.72	4527
4.0-II	4.0	63.5	1184.9	674.2	1190.6	2.295	2.458	6.64	15.70	57.70	1	18.8	18.80	4.25	4563
4.0-III	4.0	63.4	1183.2	676.9	1187.4	2.318	2.458	5.70	14.85	61.62	1.00	18.00	18.00	4	4949
Average		63.53	1181.46	674.20	1187.0	2.304	2.458	6.26	15.36	59.26	1.00	18.17	18.11	3.99	4680
4.5-I	4.5	63.43	1179.5	676.3	1186.6	2.311	2.440	5.27	15.52	66.05	1	18.66	18.66	3.74	3505
4.5-II	4.5	63.83	1182.9	681.3	1188.3	2.333	2.440	4.38	14.73	70.27	0.99	18.37	18.19	3.09	5268
4.5-III	4.5	63.13	1185.1	683.4	1192.1	2.330	2.440	4.52	14.86	69.56	1	18.01	18.01	3.83	4517
Average		63.5	1182.5	680.3	1189.0	2.325	2.440	4.72	15.04	68.62	1.00	18.35	18.29	3.55	4893
5.0-I	5.0	63.2	1196.5	689.4	1201.9	2.335	2.422	3.63	15.12	76.02	1	17.67	17.67	4.35	4050
5.0-II	5.0	64.23	1194.5	684.3	1199.7	2.318	2.422	4.33	15.74	72.50	0.98	16.34	16.01	4.67	4392
5.0-III	5.0	63.9	1185.3	685.5	1191.9	2.341	2.422	3.38	14.90	77.33	0.99	16.52	16.35	4.91	4244
Average		63.8	1192.1	686.40	1197.8	2.331	2.422	2.65	15.25	75.286	0.990	16.84	16.68	4.64	4229
5.5-I	5.5	64.1	1192	690	1199.3	2.340	2.405	2.69	15.36	82.48	0.98	15.97	15.65	5.03	3635
5.5-II	5.5	63.23	1200.5	692.9	1206.6	2.337	2.405	2.84	15.48	81.68	1.00	17.08	17.08	4.28	4373
5.5-III	5.5	63.63	1193.6	690.7	1198.3	2.351	2.405	2.23	14.96	85.07	1.0	16.45	16.29	4.79	4178
Average		63.7	1195.4	691.2	1201.4	2.343	2.405	2.59	15.27	83.08	0.99	16.50	16.34	4.70	4062.0
6.0-I	6.0	62.87	1187.6	684.6	1190.8	2.346	2.388	1.76	15.60	88.72	1.01	14.89	15.04	6.17	3311
6.0-II	6.0	64.6	1213.8	700.4	1217.3	2.348	2.388	1.67	15.52	89.23	0.97	13.99	13.57	6.65	2608
6.0-III	6.0	63.67	1200.7	694.1	1203.9	2.355	2.388	1.38	15.27	90.98	0.99	14.78	14.63	6.61	4311
Average		63.7	1200.7	693.03	1204	2.350	2.388	1.603	15.47	89.64	0.99	14.55	14.41	6.48	3410

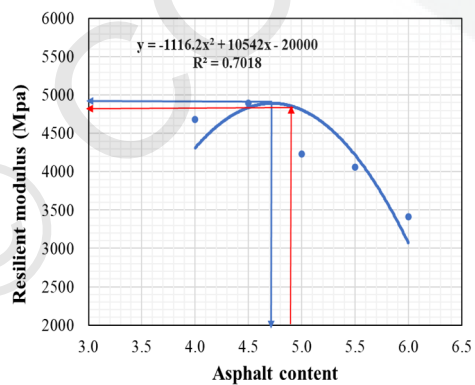
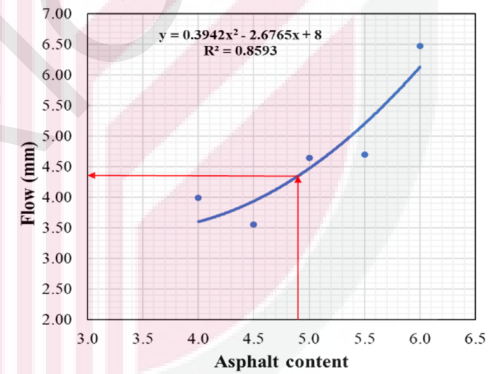
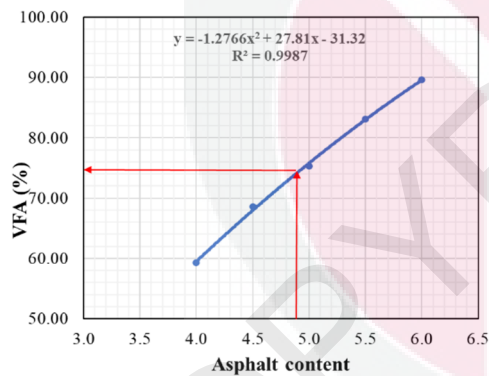
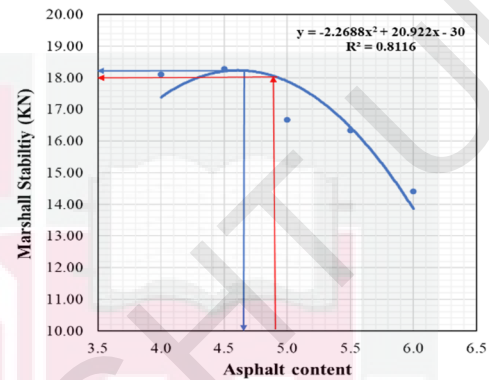
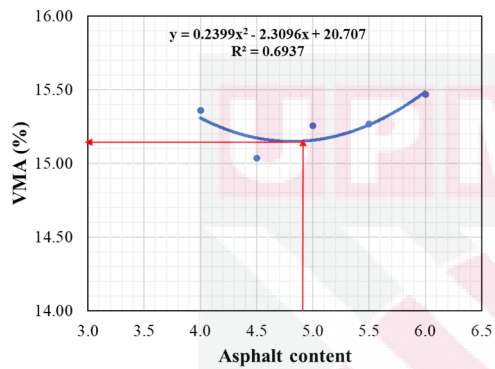
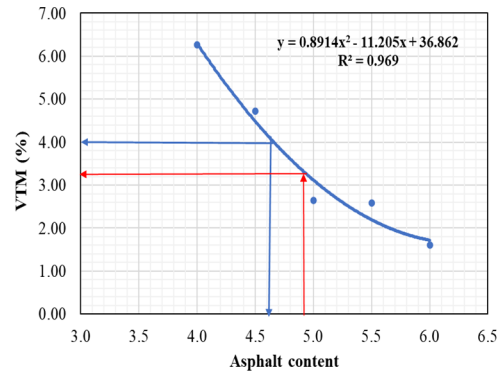
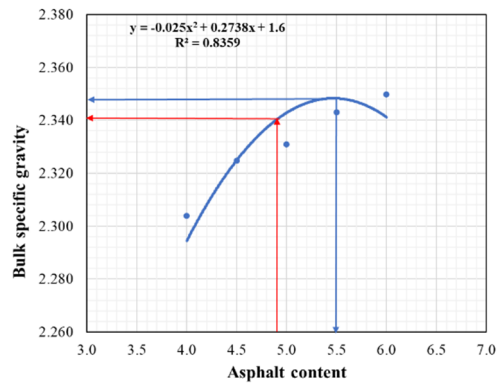


Figure B4: Optimum bitumen content determination plots for 50:50-5%

Table B8: Marshall mix design results of 50:50-5%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.89	-
Bulk density	2.341	-
Stability (KN)	18.05	>8KN
VTM (%)	3.378	3-5%
VMA (%)	15.14	>15%
Resilient Modulus (Mpa)	4858.75	>2500
Flow (mm)	4.341	2.0-4.0 (mm)
VFA (%)	74.18	70-80%



Table B9: Volumetric properties of 50:50-10% mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)		Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA				
4.0-I	4.0	63.7	1184.6	676.9	1189.7	2.310	2.456	5.96	15.13	60.61	16.4	16.24	4.8	3289
4.0-II	4.0	63.3	1181.7	672.9	1187.7	2.295	2.456	6.55	15.67	58.16	18.48	18.48	3.93	4377
4.0-III	4.0	63.9	1183.2	671.4	1190.9	2.278	2.456	7.28	16.32	55.39	18.59	18.40	4.87	3938
Average		63.64	1183.16	673.73	1189.4	2.294	2.456	6.60	15.71	58.05	17.82	17.71	4.53	3868
4.5-I	4.5	63	1187.2	682.5	1192.6	2.327	2.439	4.56	14.94	69.49	20.15	20.35	5	3738
4.5-II	4.5	64.2	1187.8	681.4	1197.5	2.301	2.439	5.62	15.89	64.62	17.49	17.14	4.2	3219
4.5-III	4.5	63.53	1193.1	686.9	1199.4	2.328	2.439	4.53	14.92	69.61	17.49	17.32	3.88	2844
Average		63.6	1189.4	683.6	1196.5	2.319	2.439	4.90	15.25	67.91	18.38	18.27	4.36	3267
5.0-I	5.0	63	1182.9	678.9	1187.6	2.325	2.421	3.95	15.46	74.48	17.89	18.07	4.44	2960
5.0-II	5.0	63.6	1202.7	691.9	1205.1	2.344	2.421	3.19	14.80	78.41	18.34	18.16	4.08	3800
5.0-III	5.0	63.4	1203	693.9	1207.4	2.343	2.421	3.23	14.83	78.24	18.8	18.80	4.46	2791
Average		63.3	1196.2	688.23	1200.0	2.337	2.421	3.46	15.03	77.041	18.34	18.34	4.33	3184
5.5-I	5.5	63.67	1195.7	688.8	1198.7	2.345	2.403	2.43	15.19	83.99	17.85	17.67	4.92	2949
5.5-II	5.5	62.6	1184.5	682.5	1189.4	2.337	2.403	2.77	15.49	82.09	17.42	17.94	4.87	2944
5.5-III	5.5	64.2	1212.4	700.9	1216.2	2.353	2.403	2.11	14.91	85.87	16.92	16.58	5.86	2848
Average		63.5	1197.5	690.7	1201.4	2.345	2.403	2.44	15.20	83.98	17.40	17.40	5.22	2913.7
6.0-I	6.0	64.8	1217.6	701.2	1219.7	2.348	2.386	1.59	15.52	89.75	12.97	12.45	6.57	2404
6.0-II	6.0	64.57	1213.2	700.3	1217.1	2.348	2.386	1.62	15.55	89.56	15.19	14.73	6.59	2455
6.0-III	6.0	64.4	1206.1	696.9	1208.3	2.358	2.386	1.17	15.16	92.30	15.5	15.04	7.36	2885
Average		64.6	1212.3	699.47	1215.033	2.351	2.386	1.46	15.41	90.54	14.55	14.07	6.84	2581

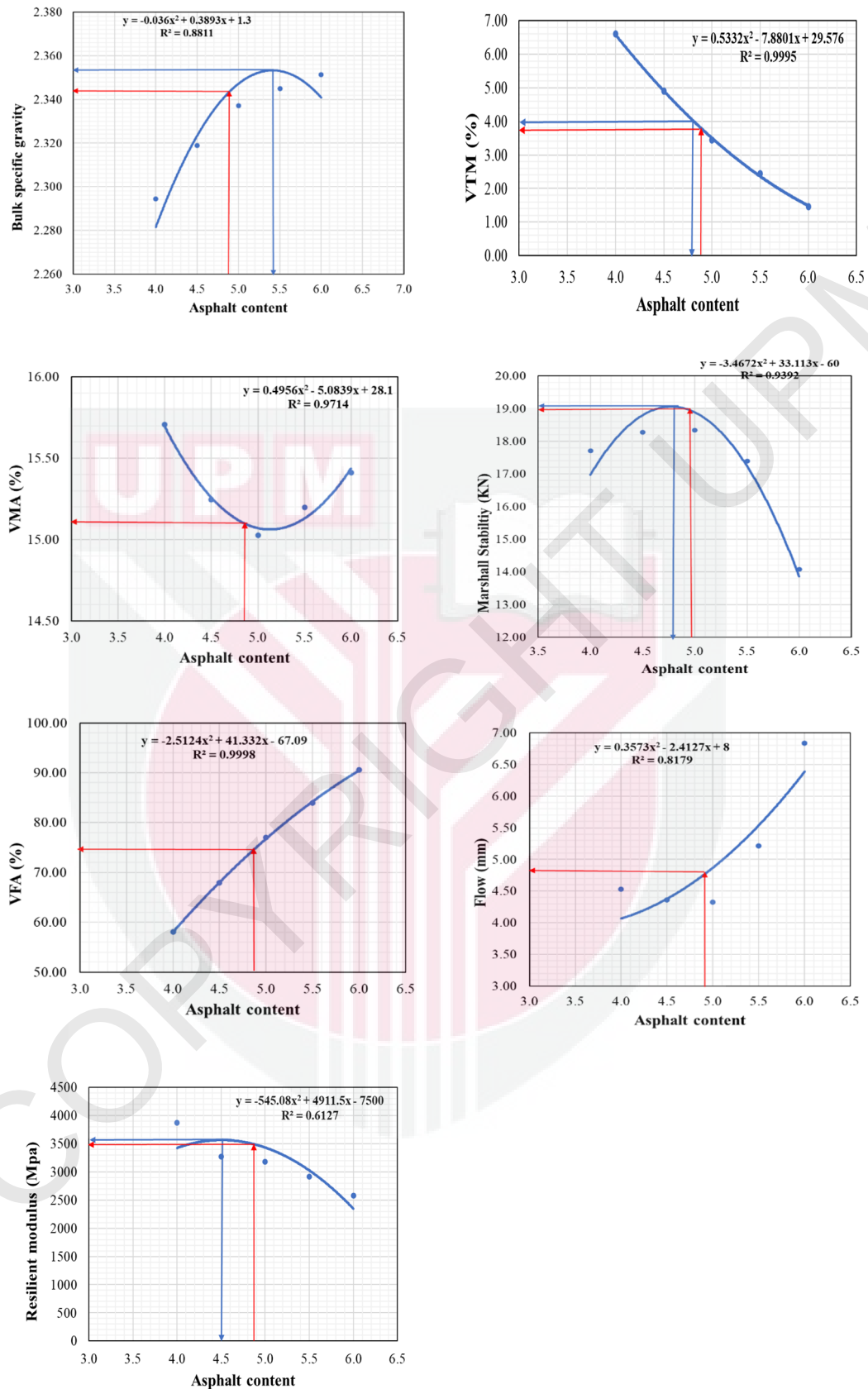


Figure B5: Optimum bitumen content determination plots for 50:50-5%

Table B10: Marshall mix design results of 45:55-10%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.88	-
Bulk density	2.342	-
Stability (KN)	19.01	>8KN
VTM (%)	3.3798	3-5%
VMA (%)	15.09	>15%
Resilient Modulus (Mpa)	3484.27	>2500
Flow (mm)	4.74	2.0-4.0 (mm)
VFA (%)	74.90	70-80%



Table B11: Volumetric properties of 50:50-15% mixture

Sample No	% AC	Sample height (mm)	Weight (g)		Specific gravity			Voids (%)			Height correlation ratio	Stability (KN)	Corrected Stability (KN)	Flow (mm)	Resilient Modulus (Mpa)
			Air	Water	Saturated	Bulk	TMD	VTM	VMA	VFA					
4.0-I	4.0	64.6	1180.5	676	1183.2	2.327	2.455	5.20	14.49	64.12	0.97	16.83	16.33	4.12	2068
4.0-II	4.0	64.7	1185.2	674.8	1186.4	2.317	2.455	5.64	14.89	62.11	0.97	16.2	15.71	4.94	2489
4.0-III	4.0	63.7	1180.2	673.3	1182.8	2.316	2.455	5.65	14.90	62.07	0.99	16.29	16.13	3.33	2035
Average			1181.96	674.70	1184.1	2.320	2.455	5.50	14.76	62.77	0.98	16.44	16.06	4.13	2197
4.5-I	4.5	64.43	1188.3	686	1190.5	2.355	2.437	3.35	13.91	75.92	0.97	16.2	15.71	5	3878
4.5-II	4.5	64.17	1190.1	683.3	1192.9	2.335	2.437	4.17	14.65	71.51	0.98	17.15	16.81	3.92	3425
4.5-III	4.5	64	1186.8	680	1187.6	2.338	2.437	4.06	14.55	72.08	0.98	16.31	15.98	3.93	2113
Average			1188.4	683.1	1190.3	2.343	2.437	3.86	14.37	73.17	0.98	16.55	16.17	4.28	3139
5.0-I	5.0	63.3	1198.1	693.1	1198.6	2.370	2.419	2.03	13.83	85.32	1	18.07	18.07	4.1	3380
5.0-II	5.0	62.97	1187.3	689.3	1188.3	2.379	2.419	1.65	13.49	87.78	1.01	18.84	19.03	4.03	3550
5.0-III	5.0	63.9	1200	695.9	1201.5	2.373	2.419	1.89	13.71	86.18	0.99	18.98	18.79	3.63	2405
Average			1195.1	692.77	1196.1	2.374	2.419	1.86	13.68	86.430	1.000	18.63	18.63	3.92	3112
5.5-I	5.5	63.27	1204.4	700.3	1208.4	2.370	2.402	1.30	14.27	90.87	1.00	17.13	17.13	5.74	2721
5.5-II	5.5	63.57	1199.6	694.4	1202.2	2.362	2.402	1.64	14.56	88.75	0.99	17.87	17.69	4.97	3211
5.5-III	5.5	63.67	1200.9	695	1203.5	2.362	2.402	1.67	14.59	88.57	1.0	16.72	16.55	4.95	2040
Average			1201.6	696.6	1204.7	2.365	2.402	1.54	14.48	89.40	0.99	17.24	17.12	5.22	2657.3
6.0-I	6.0	63.2	1200	694.3	1203.1	2.358	2.384	1.09	15.16	92.83	1	14.67	14.67	6.18	1587
6.0-II	6.0	64.97	1203.5	698.1	1207.6	2.362	2.384	0.93	15.03	93.78	0.96	16.27	15.62	7.61	2425
6.0-III	6.0	63.03	1200.9	695.5	1204.2	2.361	2.384	0.99	15.08	93.42	1	13.45	13.45	5.54	1509
Average			1201.5	695.97	1204.967	2.360	2.384	1.004	15.09	93.35	0.99	14.80	14.58	6.44	1840

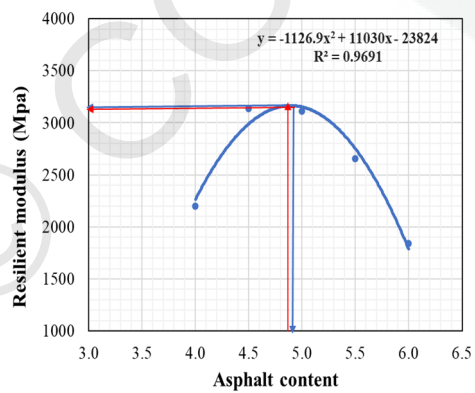
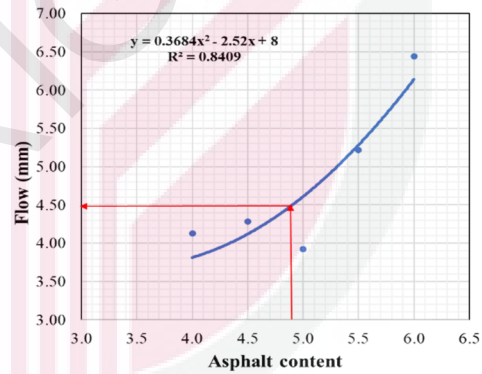
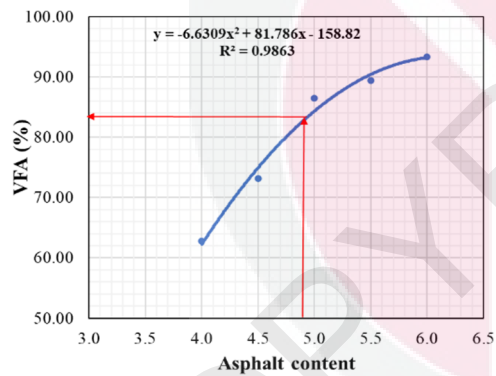
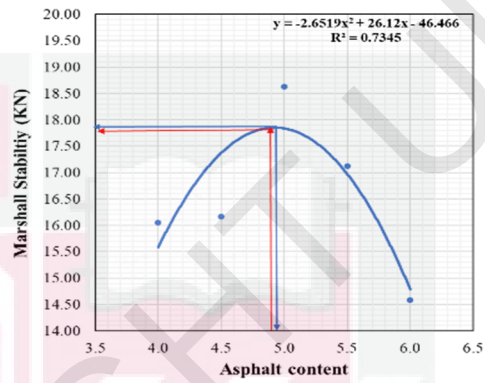
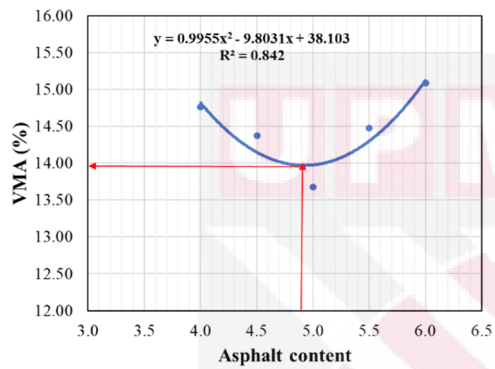
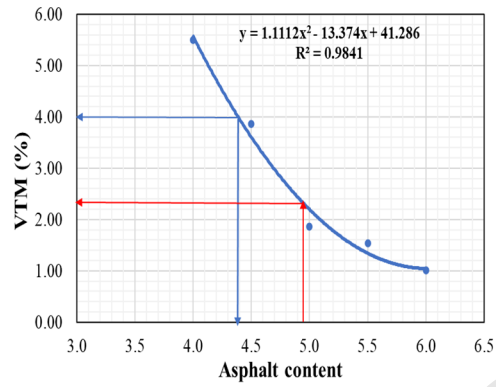
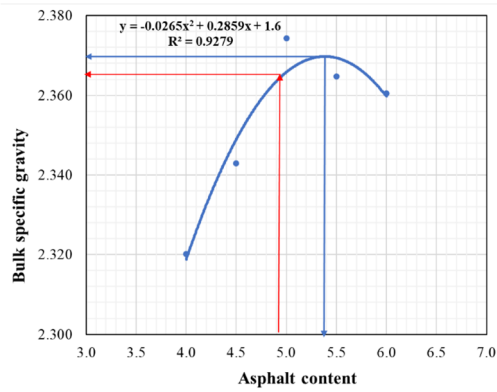


Figure B6: Optimum bitumen content determination plots for 50:50-15%

Table B12: Marshall mix design results of 50:50-15%

Marshall Properties	Values	Specifications
Optimum asphalt content (%)	4.93	-
Bulk density	2.365	-
Stability (KN)	17.85	>8KN
VTM (%)	2.402	3-5%
VMA (%)	13.96	>15%
Resilient Modulus (Mpa)	3165.78	>2500
Flow (mm)	4.51	2.0-4.0 (mm)
VFA (%)	82.93	70-80%



Appendix C

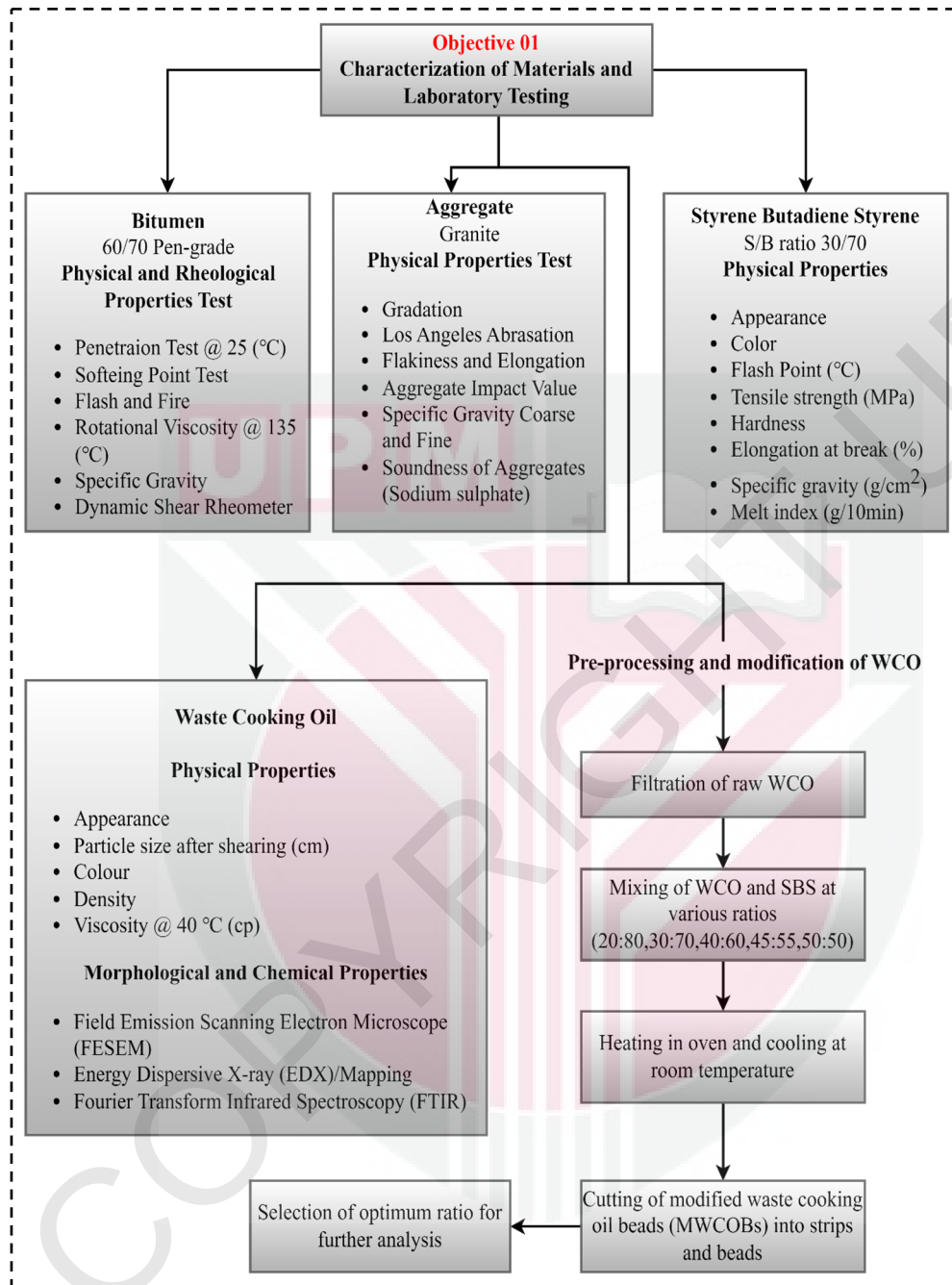


Figure C1: Detailed flow chart Objective 1 of study

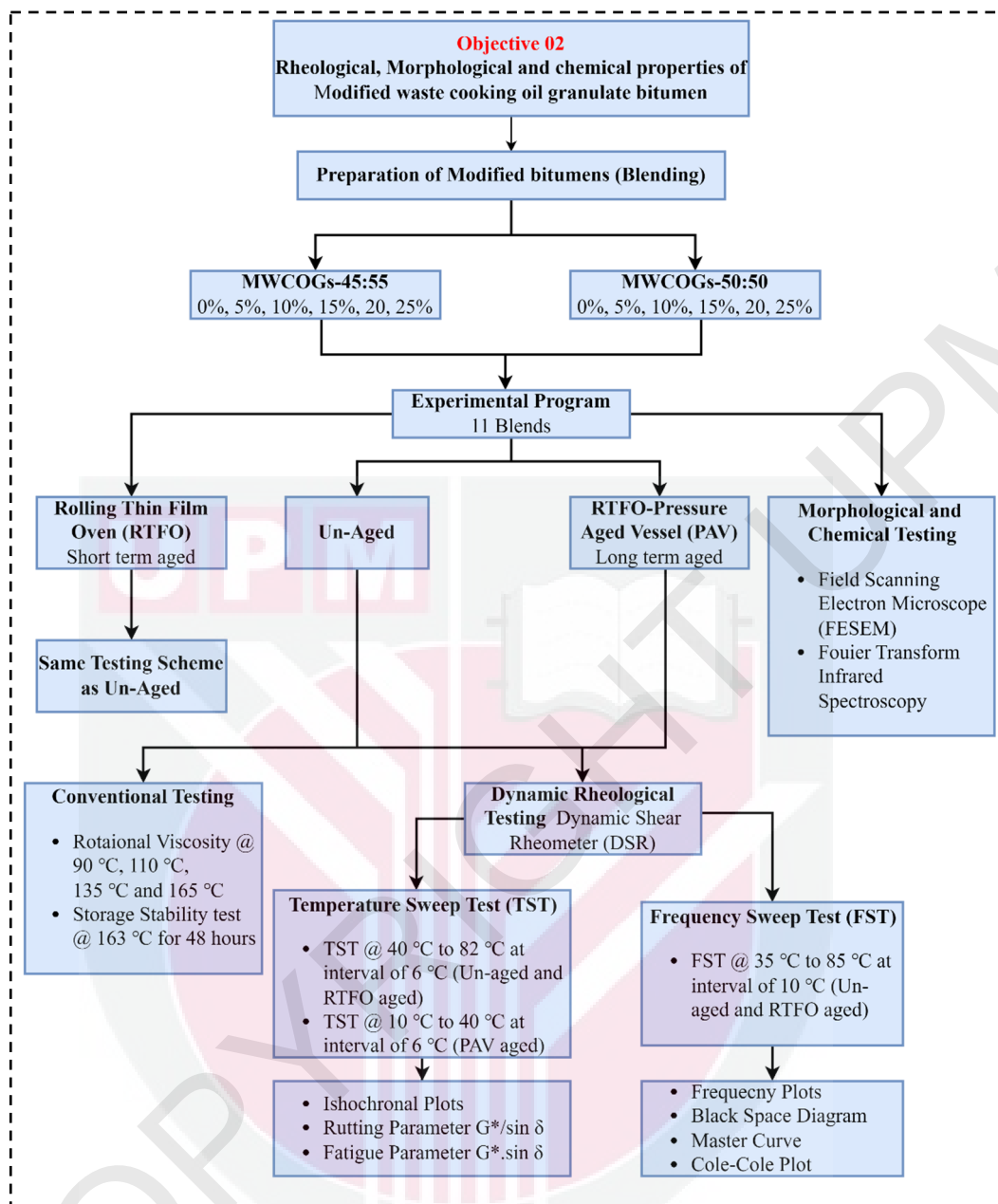


Figure C2: Detailed flow chart Objective 2 of study

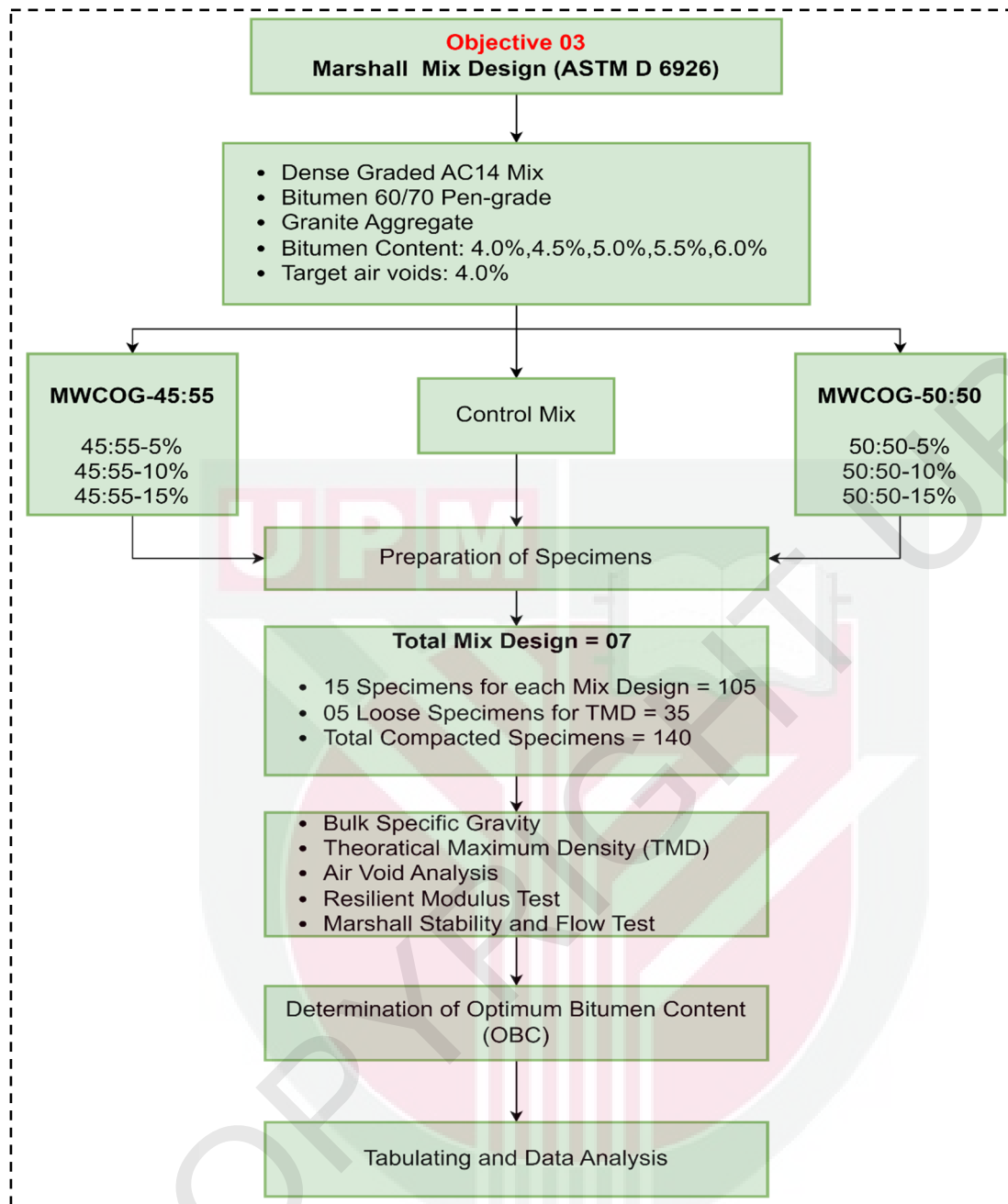


Figure C3: Detailed flow chart Objective 3 of study

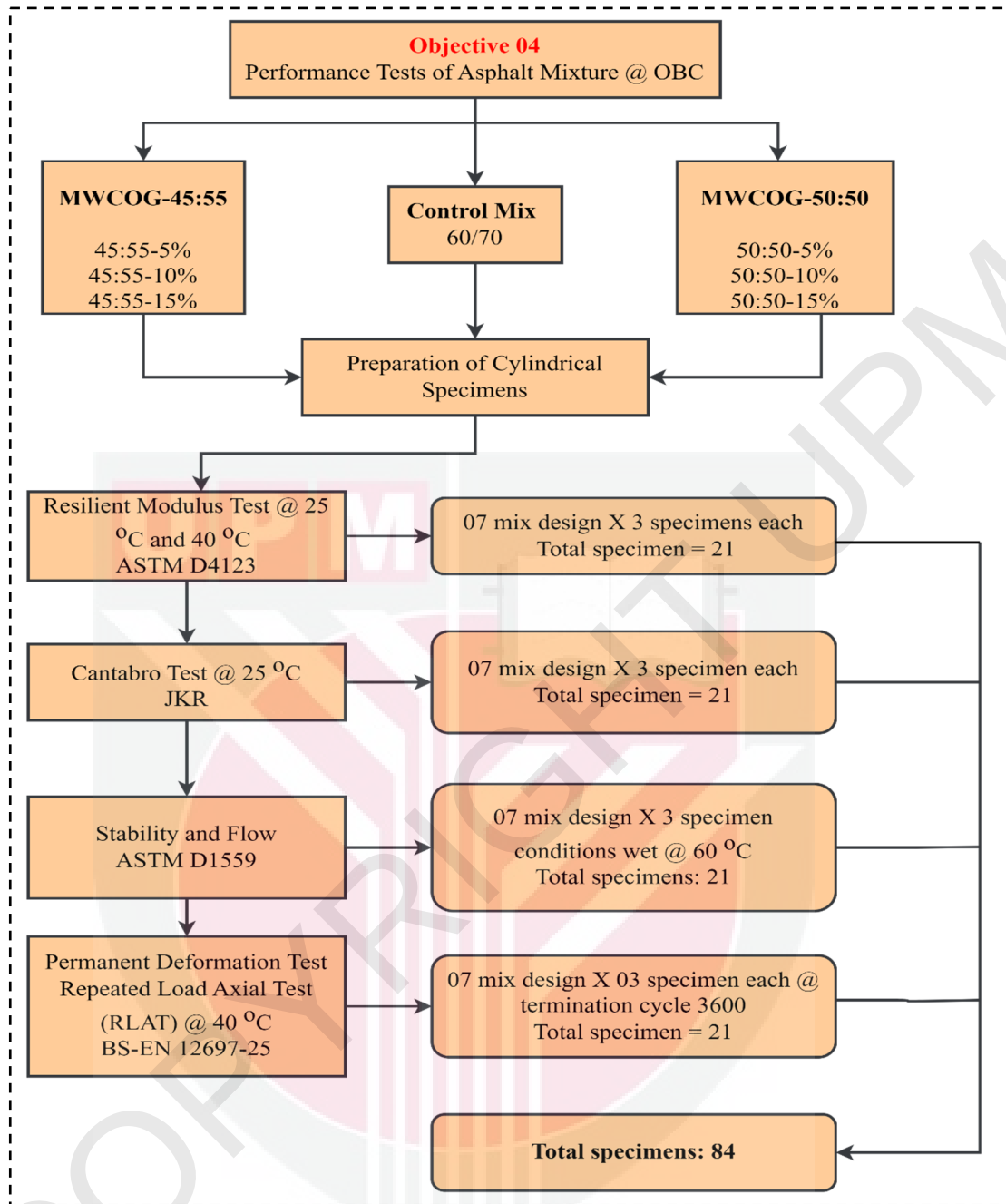


Figure C4: Detailed flow chart Objective 4 of study

LIST OF PUBLICATIONS

Journal Publications

Elahi, Z., Mohd Jakarni, F., Muniandy, R., Hassim, S., Ab Razak, M. S., Ansari, A. H., & Ben Zair, M. M. (2021). Waste cooking oil as a sustainable bio modifier for asphalt modification: A review. *Sustainability*, 13(20), 11506.

Elahi, Z., Jakarni, F. M., Muniandy, R., Hassim, S., Ab Razak, M. S., & Ansari, A. H. (2024). Influence of novel modified waste cooking oil beads on rheological characteristics of bitumen. *Construction and Building Materials*, 414, 134829.

