CHAPTER 5. WASTE ENGINE OIL: EFFECT OF SOURCE

5.1 Preface

Among the four rejuvenators selected in this study, waste engine is one of the rejuvenator. Engine oil is generally used to provide lubrication between moving parts in an engine of different machines, such as automobiles, two-wheelers, etc. It is mostly made up of naphthenic and aromatic hydrocarbons, sometimes esters and other chemical additives [271,272]. During usage, engine oil undergoes specific chemical changes due to its exposure to the internal combustion and wearing action of engine parts. The amount of used engine oil, commonly termed waste engine oil (WEO), is growing due to the rapid increase in vehicles and frequent maintenance or repair. Disposing of WEO on land or water is unsuitable due to the high amount of heavy metals (non-degradable components) and polycyclic aromatic hydrocarbons (PAHs) [273]. Some alternatives for disposal are using it as fuel, treating and reusing it during the production process of diesel oil, and using it as a binder for roofing tiles [199]. On the other hand, WEO also consists of several low molecular weight compounds similar to that of asphalt [198,274]. Given that both engine oil and asphalt are derived from crude oil, incorporating WEO into asphalt applications can be a practical and effective way to utilize waste engine oil [275]. When oils are incorporated into asphalt, available batch/column/ Toxicity Characteristic Leaching Procedure studies indicate low leaching of PAHs and heavy metals due to encapsulation in the binder; observed leachate concentrations are generally below regulatory limits, though early-age exposure, low pH, or unusually high oil dosages can increase release [276]. Thus recycling not only provides an additional solution to the disposal issue but also increases the economic value of WEO.

In this regard, WEO can be used an additive (popularly labelled as rejuvenator) to include high percentages of used asphalt mixture (recycled asphalt pavement materials - RAP) in the new hot mix asphalt (HMA). A rejuvenator should be able to restore the chemical and physical properties of RAP [277]. From the compositional model point of view, asphalt consists of asphaltenes (high molecular weight and polar) and maltenes (low molecular weight compounds and less polarity) [76]. With time and when asphalt gets exposed to multiple conditions such as sunlight, air, traffic, moisture etc., some portion of maltenes are transformed to asphaltenes [79,88]. These replenished low molecular compounds can be restored by the WEO. It should be noted that a rejuvenator should not only increase the maltenes phase but also dissolve and disperse the asphaltenes micelles well enough to restore colloidal stability [84,191,278,279]. Chemical composition dictates both short-term and long-term influence of rejuvenators [280]. It was reported that WEO not only restore the conventional physical properties (softening point, viscosity, and penetration) but also rheological (complex modulus, phase angle), molecular composition and microscopic properties (functional groups (carbonyl and sulfoxide) and morphology) as well [281–287]. This implies that WEO can be considered a rejuvenator and not a softener. From the performance of recycled mixes (Table 5-1), it can be concluded that WEO also helps improve the performance of recycled mixes. Most of the studies merely evaluated the impact of WEO on the performance of recycled mixes with different percentages of RAP and dosages of rejuvenators. It should be noted that source of WEO is generally a local service shop, and the quality varies from vendor to vendor and also day to day for each vendor. In service shops, it is of common practice to blend WEO collected from different vehicles and store in a single barrel. Sources of variation related to WEO are engine type and condition, mileage (before the service), presence of modifiers (dispersants, viscosity index improver, corrosion inhibitor etc.), original engine oil purity, etc. This raises the question: how would a blended engine oil, commonly available from service shops, perform as a rejuvenator compared to WEO from a uniform or single source? However, no study has yet addressed this concern. Therefore, the present chapter aims to evaluate the difference between a blend of used engine oils and WEO from a single, uniform source.

Table 5-1 Performance of recycled mixes with Waste Engine Oil as rejuvenator

Reference	**RAP percentage (%)**	**WEO details**	**Effect of WEO**
[288]	25 and 45	Collected from local auto repair shop	• Fatigue performance improved • Rutting resistance decreased
[289]	25, 50 and 75	Collected from local car service centre	Rutting resistance decreased
[139]	10, 20, 30 and 40	Not specified	Moisture resistance increased (till 6%)
[290]	25, 50 and 75	Collected from car service centre	By comparing with the virgin mix • Rutting resistance increased • Fatigue resistance improved (except at 25%)
[291]	10, 20, 30, 40 and 50	• Modified rejuvenator (WEO + furfural extract oil + epoxy resin)	With increasing RAP content • Rutting performance degraded

		- WEO – collected from cars after service of 5000-6000 km	- Moisture susceptibility increased - Fatigue resistance decreased
[292]	20, 30, 40, 50, 60 and 70	Not specified	Moisture resistance increased at all RAP contents

5.2 MOTIVATION AND SCOPE

Waste Engine Oil (WEO) is abundantly available, but its disposal is often environmentally challenging. It has also proven to be an effective and efficient rejuvenator. Many studies have evaluated the efficacy of WEO as a rejuvenator at different RAP contents and with various virgin binder types. However, when recycling a waste material, variation in the source is an important factor that can influence its applicability. Therefore, the main question addressed in the present chapter is whether a difference exists between WEO from a single source and blended engine oils. The effect of source on performance (rutting, fatigue, and moisture resistance) in recycled mixes is explored in this study.

The scope and experimental methodology of the present objective are outlined in Figure 5-1. Initially, the basic differences in terms of chemical bonding and structure between the two WEO rejuvenators—A (a blend of waste engine oils) and B (single-source WEO)—are studied using FTIR analysis. Binder blends are then prepared with different aged binder percentages (40% and 80%) and rejuvenator contents to determine the appropriate dosage. For example, 40A refers to the binder with 40% aged binder, 60% virgin binder, and rejuvenator A. Similarly, the terminologies for other combinations (80A, 40B, and 80B) can be interpreted. It should be noted that the aged binder used in this study is obtained by long-term aging of the VG 30 binder. Once the rejuvenation dosage is determined, the performance of recycled mixes is assessed for all binder blends. Given the tropical climatic conditions in India, low-temperature performance is not included in the experimental program. The focus of this study is limited to understanding the effect of the WEO source (blended vs. uniform) on the performance of recycled mixtures. Therefore, WEO properties themselves were not assessed within the experimental plan. Based on these experimental tests the following objectives are evaluated:

- Variance in WEO from two sources using FTIR spectral analysis.
- Evaluation of rejuvenator dosage at two aged binder contents (40% and 80%) using high-temperature performance grade (true fail temperature).
- Assessment of the performance (fatigue and rutting resistance) of recycled mixes prepared with WEO rejuvenators from two different sources.
- Evaluation of the influence of WEO source on the moisture susceptibility of recycled mixes at different aged binder contents.

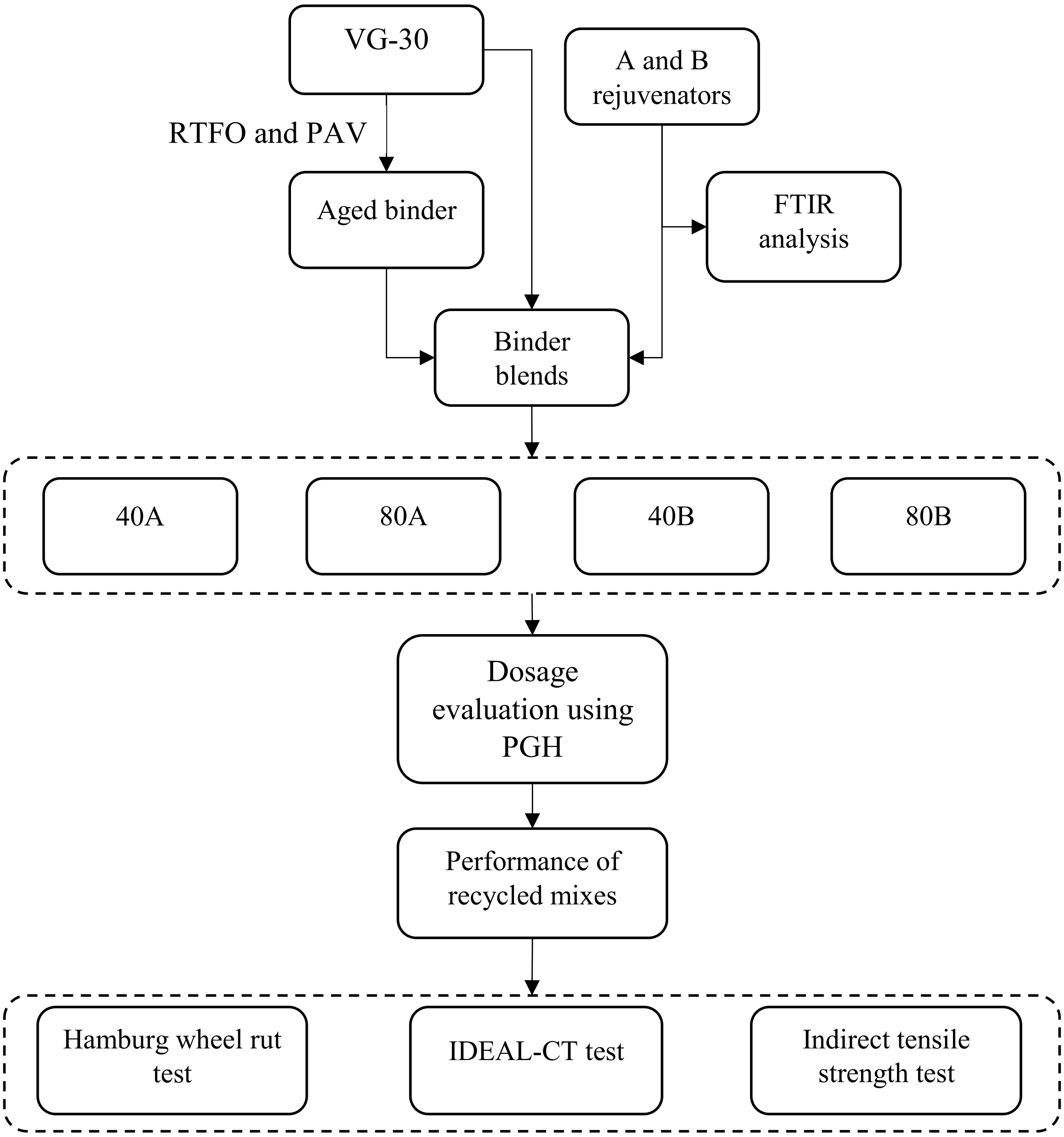


Figure 5-1 Experimental plan schematics

5.3 MATERIALS

Rejuvenator A is collected from a local service shop, and it is a blend of multiple unknown used engine oils collected from different vehicles and is of unknown age. B is acquired from a known single vehicle after using it for 2500 kilometres (approximately). Both the rejuvenators are liquid in room temperature. As already elaborated in section 3.4, Aged binder used in the study is attained by aging the VG 30 binder in the laboratory using RTFO (rolling thin film oven) [154] and one PAV (Pressure aging vessel) [155]. For PAV, time and temperature of

20hr and 100°C are used, respectively, simulating the in-field aging of 5 to 10 years [181]. It is assumed that aged binder simulated using PAV is equivalent to aged binder extracted and recovered from field RAP. For the preparation of recycled binder blends, rejuvenator is initially added to virgin binder and hand mixing is done for 15 minutes while maintaining the temperature of 125 ± 5°C. Then aged binder is mixed with the blend of virgin binder and rejuvenator using a mechanical stirrer at 2000 rpm for 20 minutes at 140 ± 5°C.

5.4 EXPERIMENTAL TESTS

FTIR test, rutting resistance (Hamburg wheel rut test), fatigue resistance (IDEAL-CT test) and moisture resistance (indirect tensile strength test) were conducted as per Sections 3.8.1.1, 3.8.1.3.2, 3.8.1.4 and 3.8.1.5 respectively. In addition, high temperature performance grade test is also conducted as follows.

5.4.1 High temperature performance grade test

The comprehensive specifics of dynamic shear rheometer and high temperature performance grading is provided in the section 6.3.1.2.3. Nevertheless, details of the test are also provided in this section. High temperature performance grading is conducted to evaluate the target dosage of rejuvenators. Several approaches or methodologies have been reported in the literature [47,114,136,293] to evaluate the optimal dosage. Among them, high-temperature performance (PGH) grade is reported as a reliable approach and hence is used in the present study [114,294,295]. Dynamic shear rheometer (DSR) is used to measure PGH following ASTM D7643 [296]. For the test, 25 mm spindle with 1 mm gap between parallel plates are used to measure complex shear modulus (G^*) and phase angle (δ) at a constant strain level of 10-12%. The temperature at which $G^*/\sin \delta$ value equals 1 kPa (unaged condition), is considered the true fail temperature. Since rejuvenator dose corresponding to true fail temperature helps achieve target VG30 grade, it is considered optimum dosage in this study. Two replicas are tested for each binder blend.

5.5 RESULTS

5.5.1 FTIR Spectroscopy

FTIR spectra of A and B rejuvenators can be seen in Figure 5-2 and Figure 5-3, respectively. Peaks observed in the absorbance spectra and their relative functional groups are specified in Table 5-2. Both the rejuvenators showed strong peaks at higher frequencies of 2800-3000, which is associated with C-H stretching of alkane functional group. Additional peaks observed in both the rejuvenators are at the range of 1350-1500 are also related to alkane functional group but of C-H bending vibration. A has a unique broad peak at wave number 3400 (approx.), which is of an amine functional group, N-H stretching. Amines provide antioxidant or anti-aging effect to bitumen [83,297]. The presence of amine can be due to a modifier in one or more of the used engine oils used to make up the blended WEO (A). Thus, A can be classified as hydrocarbon (aliphatic) of an amine-based rejuvenator. In the case of B, a weak peak at the low frequency of 700 (approx.) implies the C-H rocking vibration that also belongs to the alkane group. Thus, B is a plain hydrocarbon material of aliphatic nature.

Information about the functional class and their corresponding frequency range can be found elsewhere [298,299].

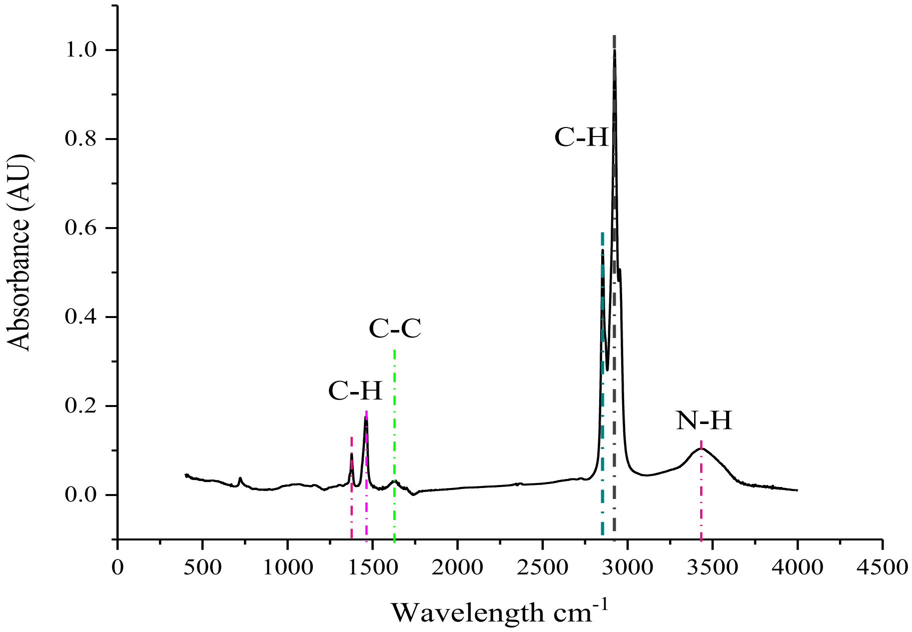


Figure 5-2 FTIR Spectra of Rejuvenator A

Table 5-2 Functional groups details

Rejuvenator	**Peaks at wave number (approx. values, cm^{-1})**	**Corresponding functional group**
A	1376	C-H (Bending vibration)
	1458	
	1629	C-C (Stretching vibration)
	2853	C-H (Stretching vibration)
	2924	
	3432	N-H (stretching vibration)
B	723	C-H (rocking vibration)
	1376	C-H (Bending vibration)
	1460	
	1597	C-C (Stretching vibration)

	2851	C-H (Stretching vibration)
	2920	

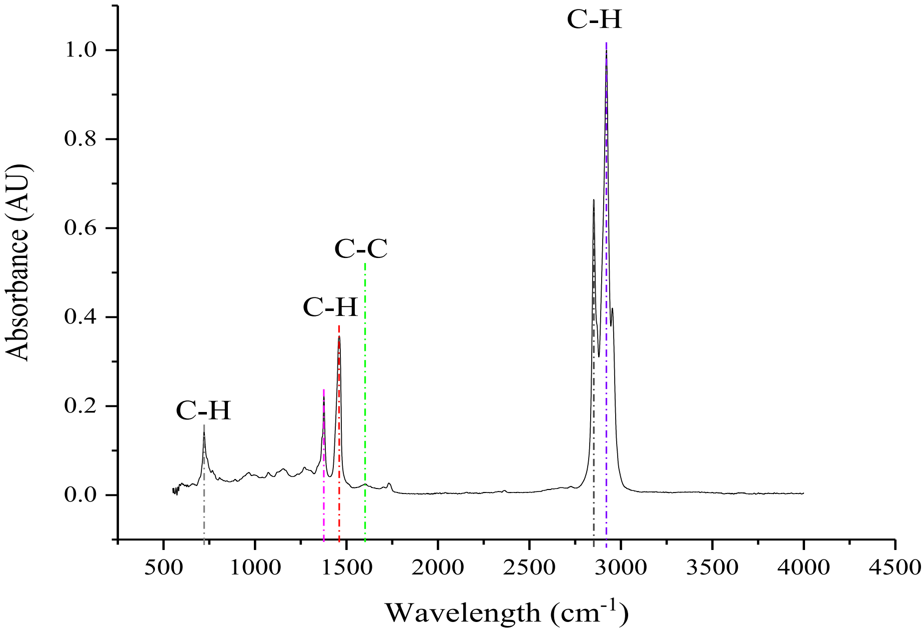
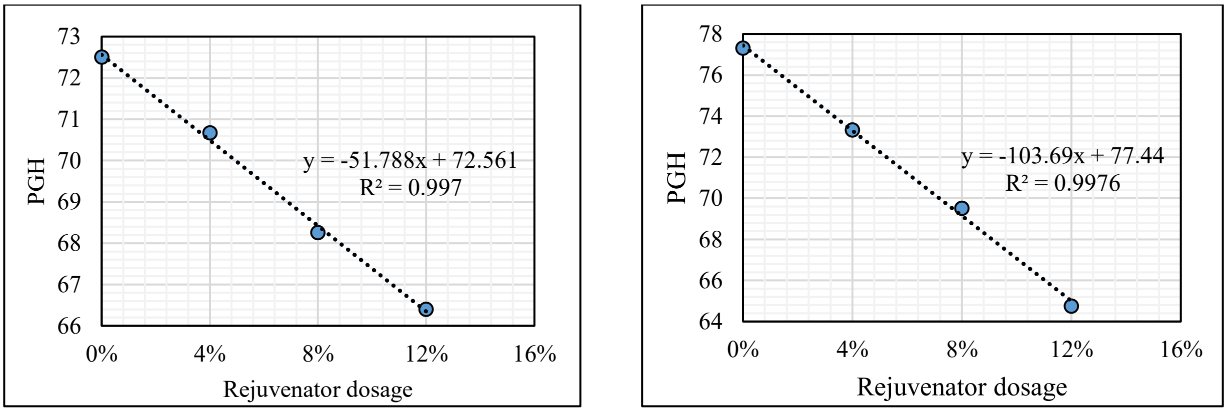


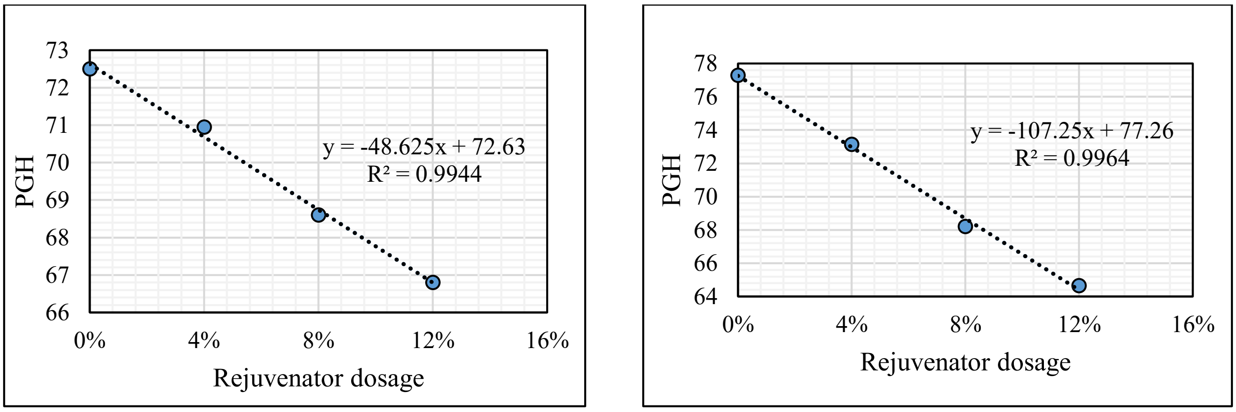
Figure 5-3 FTIR Spectra of Rejuvenator B

5.5.2 High temperature performance grade test

Binder blends with three percentages of rejuvenators, namely 4%, 8% and 12% (by weight of aged binder) are prepared to evaluate the dosage at 40% and 80% aged binder contents. For 100 gm of binder, 4% rejuvenator and 40% aged binder implies 60 gm virgin binder, 40 gm aged binder and 1.6 gm rejuvenator. Dosage in this study is defined as the amount of the rejuvenator required to match PGH (true fail temperature) of virgin binder, which is 65.5°C. PGH of the binder blends decreased linearly with the increase in quantity of rejuvenator for both the rejuvenators, as shown in Figure 5-4. At 40% RAP, it B required slightly more quantity (0.5%) than A. When the percentage of aged binder is increased, amount of rejuvenator to attain the same consistency as of VG 30 (in terms of PGH) also increases. At very high aged binder content (80%), the effect of RAP is more than the rejuvenator, thus similar dosage was obtained. But at 40% RAP content, rejuvenator type is more pronounced and dosage of A is lower than B. Amines not only provides anti-aging property but also observed to lower dosage. Rejuvenator dosage for each binder blend were 13.18% (40A), 10.92% (80A), 14.33% (40B) and 10.98% (80B). Properties of recycled binder blends are shown in Table 5-3.



(a) 40A (b) 80A



(c) 40B (d) 80B

Figure 5-4 Variation in High temperature performance grade with increase in dose for rejuvenators

Table 5-3 Properties of recycled binder blends

Property	**40A**	**80A**	**40B**	**80B**
Penetration, 0.1 mm	65.48	64.06	76.63	75.64
Softening point, °C	46.82	47.05	38.9	41.05
Zero Shear Viscosity at 60°C, poise	203.34	207.11	148.72	169.51
Kinematic viscosity at 135°C, cSt	296.2	313.5	234.8	258.2

5.5.3 Rutting performance

Rut depth after 10,000 passes, recorded by using a LVDT (linear variable differential transformer), is the parameter used to specify rutting resistance, and the results are plotted in Figure 5-5. Rut depth is the average of two samples for each binder blend. Since aggregate type and gradation is same for all the mixes, the change in the rutting resistance is due to the binder stiffness. The percentage of aged binder and rejuvenator type impacts the binder stiffness. At the same aged binder percentage, the rejuvenator type is the only source for the variation in the rutting performance. At 40% aged binder, rejuvenator A had 27.61% less rut depth than B, while 10.95% lower rutting susceptibility at 80% aged binder. Higher rut depths of recycled mixes with rejuvenator B can be due to the oily components as indicated by presence of aliphatic hydrocarbon functional group at lower frequency (723 cm^{-1}) and higher dosage [285]. It suggests that blending of engine oils from different sources can be beneficial in terms of rutting resistance. Also, rut depth increased from 2.735 mm to 3.195 mm for A and from 3.49 mm to 3.545 mm for B when aged binder content increased from 40% to 80%. Thus, rejuvenators are more predominant than aged binder at higher recycling rates.

It is worth highlighting that all recycled mixes had higher rut depth than virgin mix. This implies the excessive softening of aged binder due to the higher content of the rejuvenator than required. So, the dosage of rejuvenator corresponding to PGH will lead to poor rutting performance for recycled mixes. Though the PGH parameter was used to assess the optimum dosage of the rejuvenator, its suitability in correlating with mixture performance results was not found to be applicable in this study. Based on the binder results, it is expected that with inclusion of the optimal dosage (as evaluated considering the PGH values) of WEO the rutting resistance of recycled mixtures will match the values of the control samples (with VG30). Such softening and thereby the inferior rutting resistance of recycled mixtures highlights inability of the parameter PGH for assessment of suitable dosage of the rejuvenator.

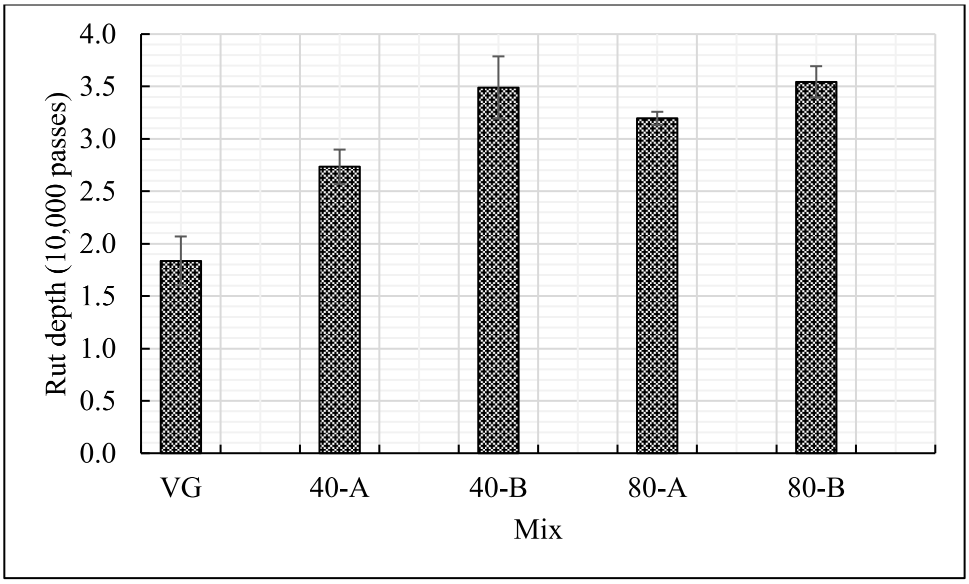


Figure 5-5 Rutting resistance of recycled mixes

5.5.4 Fatigue performance

All the recycled mixes have CT_{index} values greater than virgin mix as shown in Figure 5-6. Although dosage corresponding to PGH resulted in lower rutting performance, fatigue resistance improved. In this regard, the 40B mix with the highest rut depth showed the best fatigue resistance behaviour. Once again this can be attributed to the presence of aliphatic hydrocarbons functional groups in rejuvenator B. Therefore, a performance-based or balanced mix design would be a better approach for evaluating the dosage of rejuvenator. On the other hand, 80-A have a higher CT_{index} value than 80B despite less rut depth. This can be attributed to the blending of engine oils, which improves fatigue performance at higher percentages of aged binder. For both sources of WEO rejuvenator, increasing the percentage of aged binder leads to lower CT_{index} values, signifying the dominant role of aged binder on the fatigue resistance.

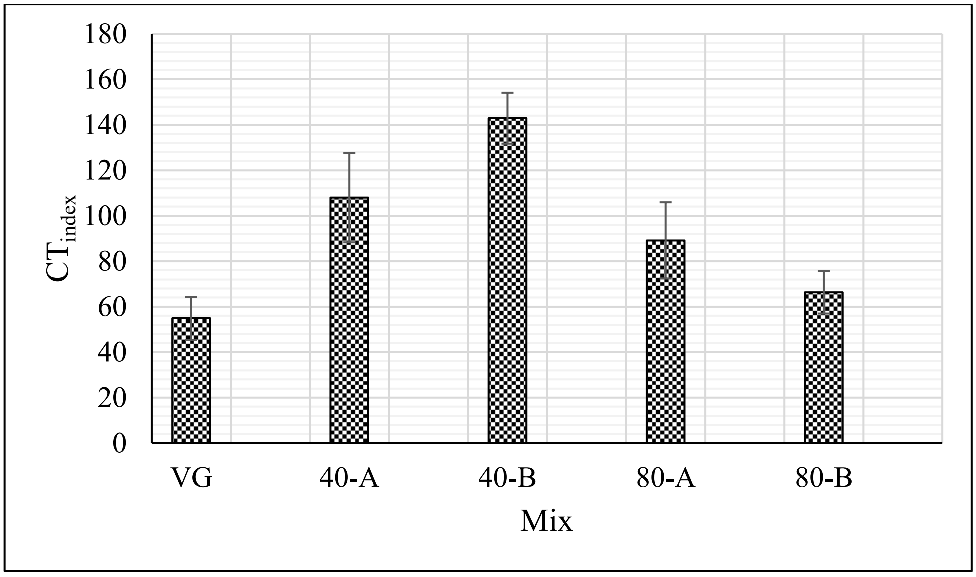


Figure 5-6 Fatigue resistance of recycled mixes

5.5.5 Moisture resistance

Results are shown in Figure 5-7. Based on the average TSR values, moisture resistance slightly improved for recycled mixes. Rejuvenator A performed better than B independent of percentage of RAP binder, confirming the benefit of blending of engine oils from different sources. Better moisture resistance of rejuvenator A can be attributed to the presence of N-H (amine) in its structure, which is basic component of anti-stripping agents [300–302]. For the same type of rejuvenator, increasing the percentage of aged binder reduced TSR value. Since aggregate type and gradation are the same for all the mixes, this can be attributed to either decreased adhesion (between aggregate and binder) or cohesion (within the bitumen mastic) due to aged binder. The rejuvenator helps lower the negative effect of aged binders since all recycled mixes had TSR (average) values higher than VG.

Nonetheless, a sharp fall in both ITS_{dry} and ITS_{wet} for recycled mixes compared to virgin mix is observed. This is due to the soft binder, which is also observed in the rutting and fatigue test results. However, there is not much difference in the values among the recycled mixes (40A, 40B, 80A and 80B). Rather than the rejuvenator type and percentage of aged binder, dosage of rejuvenator plays a key role on the tensile strength of recycled mixes. Therefore, parameter for evaluating the dosage of rejuvenator should be selected cautiously. It should be highlighted that ITS values are more sensitive than TSR when a recycled mix is compared with virgin mix (for example compare 80B with VG). It raises the question, whether considering only TSR will provide the effect of aged binder and rejuvenator on moisture performance or not. It can be interpreted in this way that the change (loss) in the maximum tensile load sustained with and without the presence of moisture will not change much, but the amount of load sustained will be affected drastically. This needs to be studied further.

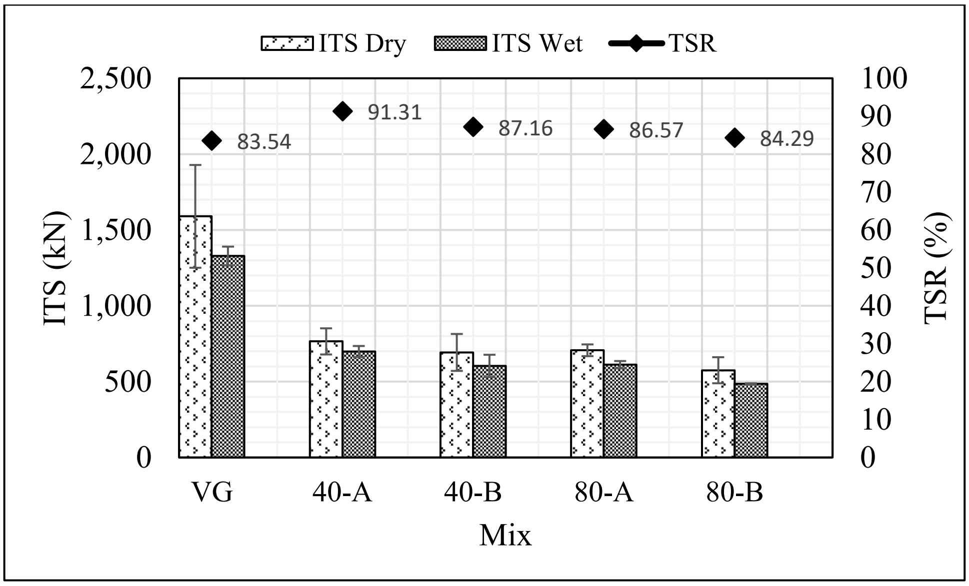


Figure 5-7 Moisture resistance of recycled mixes

5.6 ANALYSING THE EFFECT OF REJUVENTOR SOURCE AND RAP CONTENT

Two aged binder contents and two rejuvenator sources are the variables considered in this study. Binder blends are prepared and their respective influence on the performance of recycled mixes is assessed (discussed in the previous sections). In addition, two way Anova is also conducted to demonstrate the effect of the variables on the performance parameters such as rut depth, CT_{index} and TSR. Results are shown in Table 5-4. For a variable to significantly influence the response parameter, P-value should be less than 0.05 for a confidence interval of 95%.

In terms of rutting resistance, rejuvenator type is observed to have a key effect but not aged binder content, which is also highlighted in section 5.3. But this can be mainly attributed to the dosage rather than rejuvenator type. The role of aged binder (RAP content) is more dominant in case of fatigue performance. It suggests that both rejuvenators (A and B) performed similarly. Thus fatigue performance, CT_{index} here, could not capture the influence i.e., not sensitive to the rejuvenator type. However, in case of moisture resistance, neither aged binder content nor rejuvenator type influenced the TSR value. From the performance of recycled mixes, it can be suggested that rutting resistance (rut depth) will be a better indicative parameter to study the effect of rejuvenator type, source of WEO in this study.

Overall, from the performance and two way Anova results it can be concluded that rejuvenator type (source of WEO here) do not have much difference. Thus it should not be of concern if WEO is from a single source or a blend of different (unknown) used engine oils. Rather, blending unknown used engine oils slightly improves the performance of recycled mixes. It can be concluded that variability in terms of source and age cannot be a factor for disregarding WEO as a rejuvenator, based on the results of this study.

Table 5-4 Results of Two-Way ANOVA analysis

Parameter	**Source of variation**	**Sum of squares**	**Degrees of freedom**	**Mean Squares**	**$F_{calculated}$**	**P-value**
Rut depth	RAP	0.132	1	0.132	3.77	0.124
	Rejuvenator	0.61	1	0.61	17.55	0.014
	RAP×Rejuvenator	0.082	1	0.082	2.33	0.202

	Error	0.14	4	0.035		
	Total	0.965	7			
CT_{index}	RAP	4543.9	1	4543.9	20.65	0.01
	Rejuvenator	74.18	1	74.18	0.34	0.593
	RAP×Rejuvenator	1668.11	1	1668.11	7.58	0.051
	Error	879.97	4	219.99		
	Total	7166.16	7			
TSR	RAP	25.302	1	25.302	0.34	0.594
	Rejuvenator	15.327	1	15.327	0.2	0.676
	RAP×Rejuvenator	3.231	1	3.231	0.04	0.846
	Error	301.86	4	75.464		
	Total	345.71	7			

5.7 CONCLUSIONS

Waste engine oil (WEO), being a waste material, might have inconsistency or variability in the source and can influence its application as rejuvenator. So the present study is focused on evaluating the effect of source on the rejuvenating behaviour of WEO. In this regard, two rejuvenators - A (blend of multiple unknown used engine oils) and B (WEO from a known single source) are collected. FTIR test was conducted on both rejuvenators to identify the difference in chemical structure of two rejuvenators. A was found to be an amine-based aliphatic hydrocarbon, whereas B was simply a plain aliphatic hydrocarbon. The presence of amine can be due to a modifier in the blend of used engine oils that make up WEO A.

RAP used in this study is obtained from laboratory aging of VG-30 binder. The dosage of the rejuvenator at two different aged binder contents (40% and 80%) is evaluated using PGH parameter. At 40% aged binder content, the dosage for A is slightly lower than B. However, at

80%, both the rejuvenators have similar dosages. At very high aged binder content (80%), the effect of aged binder is more than the rejuvenator. But at 40% aged binder content, rejuvenator type is more pronounced. Binder blends at evaluated rejuvenator dosage are used to prepare recycled mixes. Based on the performance of the recycled mixes following conclusions can be drawn: Recycled mixes exhibited higher rut depths than virgin mixes, indicating that excessive rejuvenator content caused over-softening of the aged binder, with the PGH dosage resulting in poor rutting resistance. Despite this, all recycled mixes achieved higher CTindex values than the virgin mix, though increasing aged binder content reduced CTindex, highlighting its dominant influence. Based on TSR values, moisture resistance slightly improved for recycled mixes, with A consistently performing better than B.

Two-way ANOVA results suggests that rejuvenator type (source of WEO) have significant influence only on rut depth but not on CT_{index} and TSR. Rather than rejuvenator type, dosage influence is more on the rut depth. From the overall performance, it can be said that source of WEO do not impact the performance of recycled mixes considerably. Even so, blending unknown used engine oils slightly improves the performance of recycled mixes. Thus blended WEO is used in fulfilling the remaining objectives of the study.