CHAPTER 5

SYNERGIC EFFECT OF DETA (DIETHYLENETRIAMINE) AND STEARIC ACID ON IMPROVED STORAGE STABILITY OF CRUMB RUBBER MODIFIED BITUMEN

Crumb rubber is most commonly used for bitumen modification due to its elastic nature. However, crumb rubber modified bitumen has storage stability issue at high temperature. Thus, this study focused on improvement of storage stability of the CRM) using seven different ratios of DETA and stearic acid, i.e. 1:0, 0:1, 1:1, 1:2, 1:3, 2:1 and 3:1 to visualize the synergic effect in combination. We have prepared several CRMB blends by using above ratio of DETA and stearic acid. All Physical and rheological properties of prepared blends were carried out for this study. Meanwhile, the performance properties such as Marshall Stability, rutting properties of the desired blends have also been carried out.

5.1 INTRODUCTION

The increasing number of vehicles on the road generates billions of used tires every year in world. About 1.4 billion tires are sold worldwide each year which creates a portion of waste on earth.[96] Being non-biodegradable and production in large volume, these tires are considered to be most problematic sources of waste. Therefore, environment concern has led us to seek alternative usage of waste tires. One of the usages of these waste tires is to ground in to crumb rubber and used for the modification of bitumen. Due to high elastic properties of crumb rubber, it has been used for bitumen modification purpose for past several decades.[97] The utilization of scrap tires for bitumen modification can not only help in the conservation of natural resources but also enable the creation of high-performing asphalt pavements in comparison with conventional paving grade bitumen.

Crumb rubber is the term widely used for recycled tire rubber produced from scrap tires. Rubber from discarded tire is grinded to crumb and is mixed with bitumen to form CRMB. The utilization of scrap tires in CRMB can not only help in the safe disposal of rubberized waste but also enable the creation of high-performing bitumen pavements in comparison with conventional paving grade bitumen [98]. It has been shown by some research that the incorporation of crumb rubber into bitumen is a proper way of enhancing the performance grade (PG) of the bitumen which improves the high temperature rutting resistance and low temperature cracking. [99-103]

There are two processes for the production of crumb rubber modified bitumen one is wet process and another is dry process, but generally wet process is more used.[3] Bitumen-Rubber pavements have also been depicted to have lower maintenance costs,[4] lower noise generation,[104-106] higher skid resistance with better night-time visibility.[107] The disadvantage of using wet process is there is a chance of formation of a non-homogeneous blend.

During the storage or transportation of crumb rubber modified bitumen without agitation, phase separation occurs between the crumb rubber particles and the binder at high temperature. Due to this phase separation, most of the crumb rubber particles are settled down at the bottom of the container. The swollen rubber crumb particles are get settle down quickly due to their higher density than the bitumen phase. Sometimes migration of crumb rubber particles to the top of the storage container because of reduced density of the crumb rubber particles after swelling. So, there is a formation of unstable condition in a rubberized bitumen blend with different properties after the storage. [8-11, 80] The variation in storage stability between different modified binders is due to the variation in crumb rubber modifier compositions.[81-83]

Therefore, researchers modified the chemical bonds between the modifying agent and bituminous compound. Kocevski et al. (2012)[47] used grafting process for the improvement of CRMB properties, in which the surface of crumb rubber was modified by bulk polymerization of acrylic acid. The US Federal highway administration used chemical modifications of crumb rubber in which generation of free radicals on the surface, are used for better interactions with bitumen which improve the storage stability of the CRMB mix.[108] Yadollahi et al. (2011)[109] used polyphosphoric acid and an additive (vestanamer) to achieve cross linking between the sulphur elements and the components of bitumen to produce macropolymer network with improved properties of bitumen with improved elastic properties and lower creep stiffness at low temperatures. An activation agent like furfural was used to improve storage stability of CRMB bituminous mix.[10] Cheng et al. (2011)[110] used a polymeric compatibilizer having conjugated diene was used to produce an improved thermal cracking resistance and permanent deformation with improved storage stability of CRMB. Therefore, waste crumb rubber has drawn attention of worldwide scientists for safe, cheap and economic way for disposal.

The objective of current research is to enhance the storage stability of CRMB with addition of certain chemical modifier. For this study, we have used DETA (diethylenetriamine) and stearic acid in seven combinations, i.e.1:0, 0:1, 1:1, 1:2, 1:3, 2:1 and 3:1 to visualize the synergic effect over storage stability. With that, we have also carried out the rheological and performance properties of storage stable CRMB blends to support our findings.

5.2 RESEARCH METHODOLOGY

5.2.1 MATERIALS

VG-10 grade (viscosity grade) bitumen was obtained from Mathura Refinery, Indian Oil Corporation Limited, India was used for all experimental activities. Physiochemical properties of neat bitumen were given in Table 4.1.

Crumb rubber (CR) powder of 30 mesh size, was collected from Indian Oil Marketing Division. Physiochemical properties of CR was given in Table 4.2.

Chemicals like diethylenetriamine (DETA) (purity >99.0 %) obtained from Spectrochem and Stearic acid (purity >99.5%) were obtained from sigma Aldrich (India). All chemicals were used without any further purification.

5.2.2 BITUMEN MODIFICATION PROCEDURE

For this, we have initially optimized the bitumen modification using various combinations of bitumen, DETA and stearic acid (0.1, 0.3 and 0.5 wt. % of bitumen) with 10% of crumb rubber as a base material. After optimization of additives at 0.3 wt. %, bitumen was blended with 10% crumb rubber at 160-170 $^{\circ}$C for 1 h to prepare CRDS-1. Similarly, different blends were prepared by consecutive addition of 0.3% DETA to prepared CRDS-2, CRDS-3, CRDS-4 CRDS-5 CRDS-6 CRDS-7 and CRDS-8, in which the ratio of DETA and stearic acid was, i.e.1:0, 0:1, 1:1, 1:2, 1:3, 2:1 and 3:1 respectively

5.3. RESULTS AND DISCUSSION

5.3.1 PHYSICAL PROPERTIES

The neat bitumen and prepared blends viz: CRDS-1, CRDS-2, CRDS-3, CRDS-4, CRDS-5, CRDS-6, CRDS-7 and CRDS-8 blends were subjected to penetration, softening point, elastic recovery and viscosity and separation test as per ASTM test method described in Chapter-3. The results of these tests are given in (Table 5.1).

We have found that penetration depth ranged from 44 to 86 dmm, CRDS-4 has lowest penetration, i.e. 44 dmm, which was decreased from CRDS-1, i.e. 86 dmm respectively. However, penetration of other crumb rubber modified blends was found to comparable with CRDS-1. Similarly, softening point of modified crumb rubber modified have increased from neat bitumen and ranged from 46 to 57 °C. Softening points of all CRMB blends are improved compare to CRDS-1. However, the separation value of CRDS-4 was found to be the lowest one, i.e. 2.4 °C compares to all CRMB blends. Elastic recovery (ER) of all modified bitumen blends were found to be increased from CRDS-1. It is cleared from Table 5.1, that the rotational viscosities of all modified bitumen at 150 °C decreases in comparison to CRDS-1. Incorporation of DETA and Stearic acid play an important role to decrease the viscosity of modified bitumen which may further helps to improve rheological properties of crumb rubber modified bitumen

5.3.1.1 STORAGE STABILITY TEST

The storage stability is one of the required criteria to use previously prepared and the separation of CRMB's under storage. The storage stability data of CRMB blends are shown in (Figure 5.1).

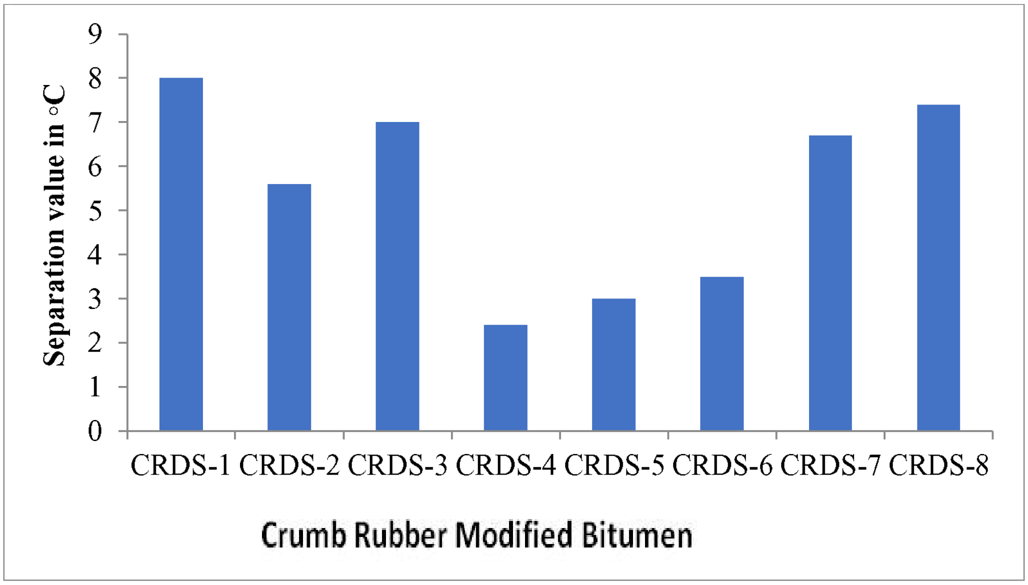

Figure 5.1: Separation value of different CRMB blends

Table 5.1: **Physical properties of modified bitumen**

Sample code	**% of VG-10**	**% of CR**	**% of DETA**	**% of Stearic acid**	**Penetration in dmm**	**Softening Point in °C**	**ER@ 15°C in %**	**Viscosity@ 150°C in Poise**	**Separation Value in °C**
Neat Bitumen	100	-	-	-	86	46	15	1.63	-
CRDS-1	90	10	-	-	47	56	70	6.28	8.0
CRDS-2	89.7	10	0.3	-	46	57	75	6.00	5.6
CRDS-3	86.7	10	-	0.3	46	57	73	5.60	7.0
CRDS-4	89.4	10	0.3	0.3	44	57	76	5.50	2.4
CRDS-5	89.1	10	0.3	0.6	45	57	75	5.45	3.0
CRDS-6	88.8	10	0.3	0.9	45	57	75	5.30	3.5
CRDS-7	89.1	10	0.6	0.3	46	57	75	4.51	6.7
CRDS-8	88.2	10	0.9	0.3	46	57	75	4.57	7.4

The test results indicated that increase in the percentage of stearic acid and DETA increases the separation value of the modified blend (Figure 5.1). It is cleared that the 1:1 combination of DETA and stearic acid (CRDS-4) gives lowest separation value i.e. 2.4 °C. As increase the concentration of Stearic acid i.e. 1:2 and 1:3 combination of DETA and Stearic acid (CRDS-5 and CRDS-6), the separation value increases from 2.4 (CRDS-4) to 3.0 and 3.5 °C. Again, when the concentration of DETA increased i.e. 2:1 and 3:1 combination of DETA and Stearic acid (CRDS-7 and CRDS-8), the separation value increases from 2.4 (CRDS-4) to 6.7 and 7.4 °C. It is known that lower the separation value, higher the storage stability. So CRDS-4 has better storage stability compared to others.

In 1:1 combination of DETA and stearic acid both these additives may react with each other and forms long chain amide molecules. The crumb rubber particles may be entangled within this long chain amide structure inside the body of bitumen. This leads to increase in storage stability of CRMB. As we further increase DETA or Stearic acid, storage stability of CRMB was again found to decreases. This may be attributed due to complete reaction of DETA with doped stearic acid molecules then excess unreacted DETA molecules may separates from bitumen because of its lower density (0.95 g/cm^3) than bitumen (1.03 g/cm^3).

5.3.2 RHEOLOGICAL PROPERTIES

5.3.2.1 DYNAMIC SHEAR RHEOMETER (DSR) Test

This test is generally used to characterize the deformation and elastic behaviour of bitumen binders at different temperatures. All the DSR testing was performed on Anton Paar MCR102 by using the method AASHTO T315-10 described in chapter 3. The behaviour of all unaged modified bitumen has shown in Figure 5.2 and the RTFO aged modified bitumen are shown in Figure 5.3.

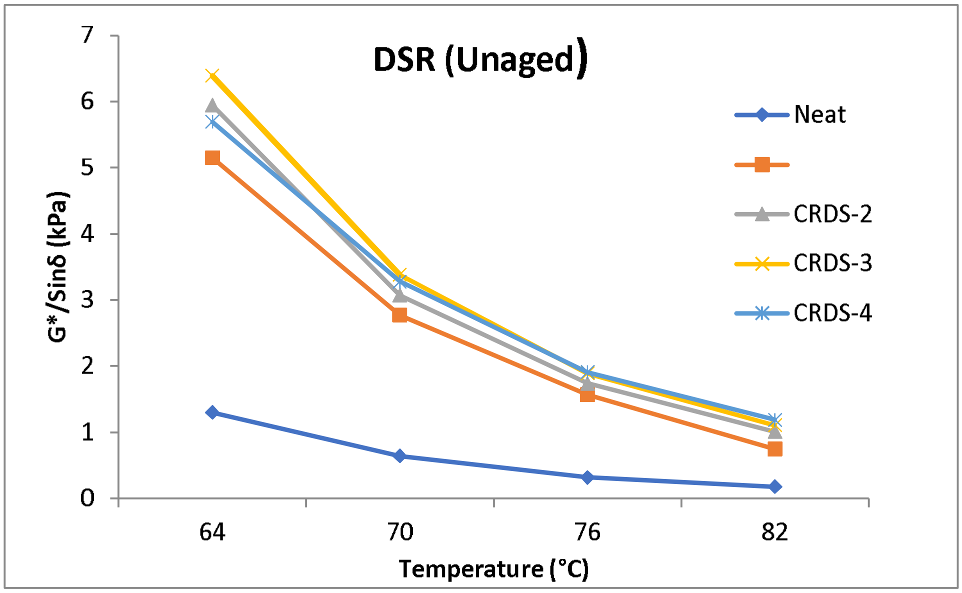

Figure 5.2: G*/Sinδ (kPa) value at different temperature for unaged binder

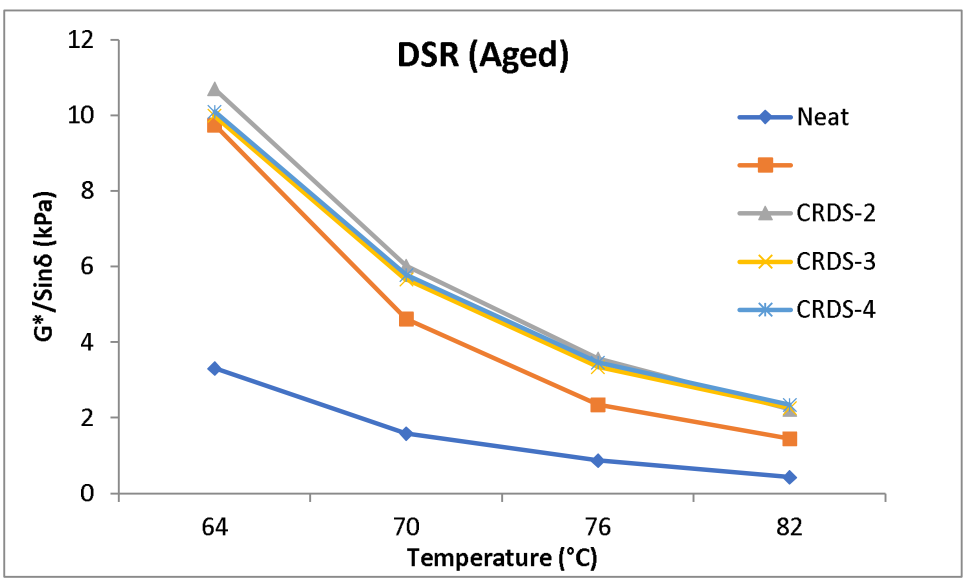

Figure 5.3: G*/Sinδ (kPa) value at different temperature for RTFO aged binder

We have studied the rheological properties of neat, CRDS-1, CRDS-2, CRDS-3, and CRDS-4 to observe the synergic effect of both dopped additives on rheological properties of CRMB. G*/Sinδ for unaged samples of CRDS-1, CRDS-2, CRDS-3, and CRDS-4 were found to have 0.75, 1.01, 1.11 and 1.19 kPa respectively at 82 °C. The acceptable value for unaged binder as per AASHTO T315-10 standard is the value should be ≥ 1 kPa. Thus, all RTFO aged modified blends (CRDS-1, CRDS-2, CRDS-3, and CRDS-4) were found to possess acceptable value for G*/Sinδ, except CRDS-1.

G*/Sinδ for RTFO aged samples of CRDS-1, CRDS-2, CRDS-3, and CRDS-4 were found to have 1.45, 2.23, 2.26 and 2.35 kPa respectively at 82 °C. Among all the prepared RTFO aged CRMB samples (CRDS-1, CRDS-2, CRDS-3, and CRDS-4) were found to possess acceptable value for G*/Sinδ, except CRDS-1, which is less than 2.2 kPa. The acceptable value for RTFO aged binder as per AASHTO T315-10 test method is the value should be ≥ 2.2 kPa.

In the present work, CRDS-4 was found to have highest value for G*/Sinδ 1.19 for unaged and 2.35 kPa for aged binder as compared to others as well as neat bitumen.

5.3.2.2 BENDING BEAM RHEOMETER (BBR)

The low temperature stiffness and relaxation characteristics of bitumen binders are measured by BBR test. From this test, the ability to resist low temperature cracking of the binder can be determined. The test was carried out as per AASHTO T313-10 test method described in chapter 3.

The stiffness value mentioned in Figure 5.4 for CRDS-1, CRDS -2, CRDS -3 and CRDS -4 blends were comes out to be 243, 169, 175 and 173 at -18 °C, which is less than 300 to be required for passing the sample as per AASHTO T313-10 test method.

The m-value in Figure 5.5 showed that CRDS-1, CRDS -2, CRDS-3 and CRDS-4 blends were coming out to be 0.281, 0.289, 0.317 and 0.331 at -18 °C. The m-value should be more than 0.3 to be required for passing the sample as per AASHTO T313-10 test method. Thus CRDS-3 and CRDS-4 blends are passed at -18 °C.

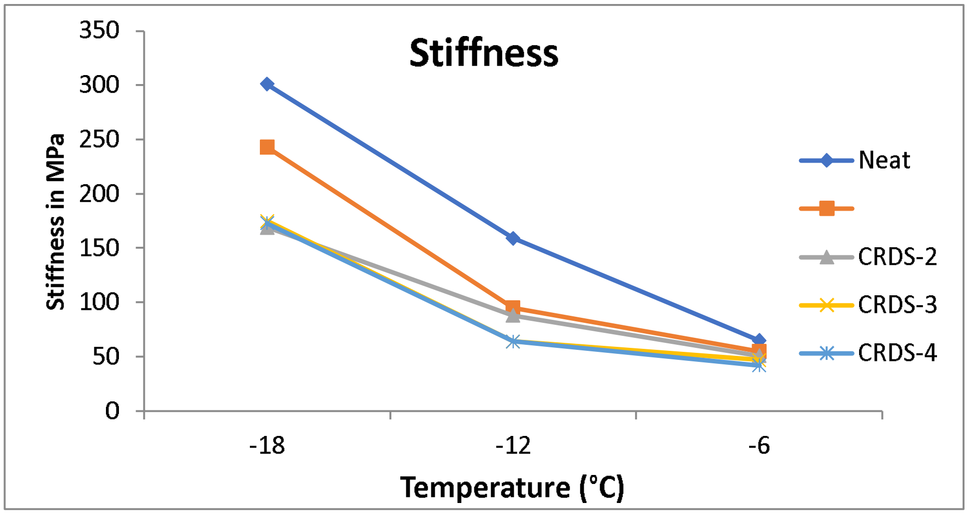

Figure 5.4: Stiffness of CRMB at different temperature

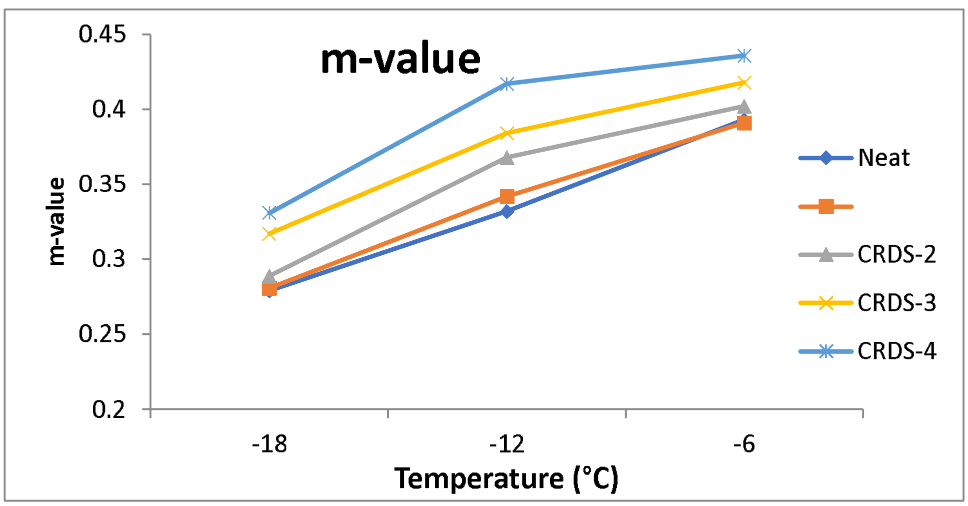

Figure 5.5: m-Values of CRMB at different temperature

It was found that CRDS-4 have best stiffness values and m-values at different temperature as compared to rest other blends as well as neat bitumen which showed that CRDS-4 will have good low temperature thermal cracking resistance as compared to others. This may be due to formation of long chain amide molecule inside the body of bitumen. In rest of the other prepared blends both storage stability and rheological properties was not as good as in case of CRDS-4. This shows that synergic effect of additive play an important role in bituminous matrix. The results also reflect that, the long chain amide formation inside the body of bitumen may enhance storage stability as well as other rheological properties. Therefore, we have selected only CRDS-4 blend for performance evaluation studies and compared it with CRDS-1 and neat bitumen.

5.3.2.3 MULTIPLE STRESS CREEP RECOVERY (MSCR) TEST

The recoverable strain (elastic response) and Jnr (non-recoverable creep compliance) of bitumen binders or modified binders can be evaluated by this test with more accurately than conventional DSR test. The test was carried out as per AASHTO MP19-10 described in chapter 3.

The percent of recovery exhibited by diethylenetriamine with stearic acid modified CRMB binders was significantly greater than that conventional CRMB at the test temperature 64 °C (Figure 5.6). Non-recoverable creep compliance (Jnr) values in Figure 5.7, showed that at 3.2 kPa^{-1} for CRDS-1, CRDS-2, CRDS-3 and CRDS-4 blends were coming out to be 0.52, 0.41, 0.48, and 0.39 kPa^{-1} which are less than 0.5 kPa^{-1} except CRDS-1 required for extremely heavy traffic road as per AASHTO MP19-10 specification. Average percentage recovery values were also found to be greater than neat bitumen at both 0.1, 3.2 kPa^{-1} (Figure 5.7). All the test data obtained (Jnr-difference and % Recovery) after multiple stress creep recovery test showed that the prepared CRDS-4 blend will have best for extremely heavy traffic road condition.

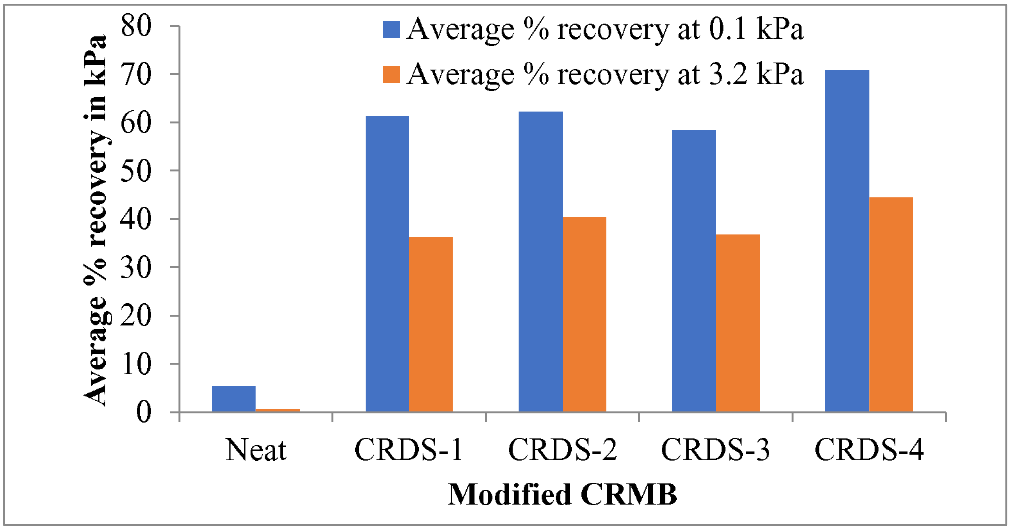

Figure 5.6: MSCR of average percentage recovery at 64 ºC

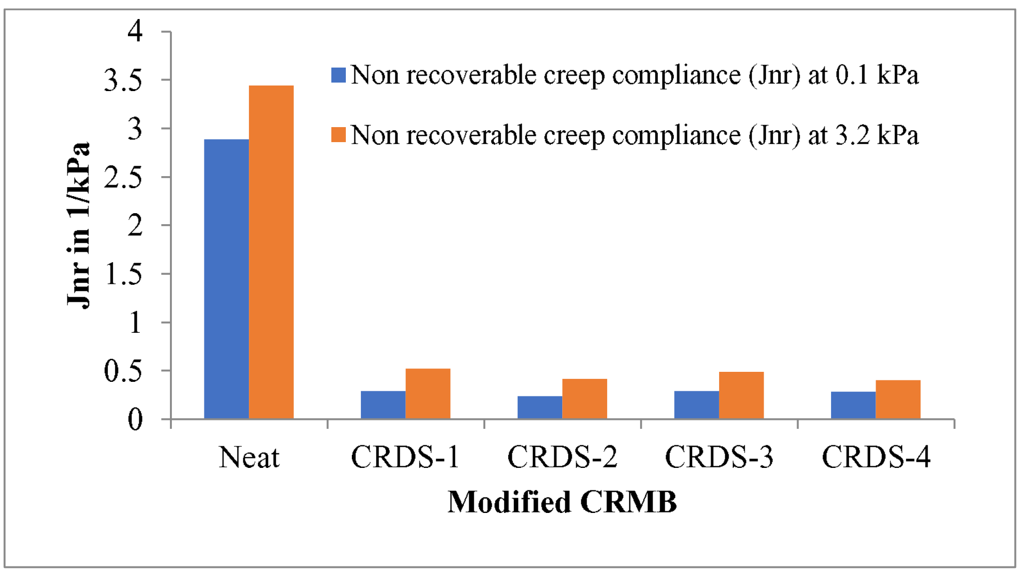

Figure 5.7: Non-recoverable creep compliance (Jnr) at 64

5.3.3 PERFORMANCE PROPERTIES

5.3.3.1 MARSHALL STABILITY TEST

This test is used to determine the Marshall Stability and flow value of the bituminous mixture specimen using Marshall apparatus. Marshall Stability represents the maximum load required for the failure of the specimen and flow value represents the total amount of deformation of the sample. Specimen samples were prepared as per ASTM D6926 and ASTM D6927 methods.

CRDS-4 was the best sample because of its better storage stability, highest G*/Sinδ value, good rutting resistance, better creep stiffness and low temperature thermal cracking resistance characteristics as compared to rest of the other prepared CRMB blends. Therefore CRDS-4 sample was investigated for Marshall Stability tabulated as Table 5.2 and test data was compared with CRDS-1 and neat bitumen.

Table 5.2: Retained Marshall Stability of bituminous mixes

Sample code	Marshall Strength (kN) before conditioning (S_1)	Flow value (cm) before conditioning	Marshall Strength (kN) after conditioning (S_2)	Flow value (cm) after conditioning	Retained Marshall Stability (%) = (S_2/ S_1) ×100
Neat Bitumen	14.84	3.29	10.16	3.66	68.46
CRDS-1	19.76	3.35	15.13	3.30	76.56
CRDS-4	22.92	3.41	19.85	3.34	86.60

Marshall Strength before and after conditioning of the sample (Table 5.2) was found to be 14.84, 19.76, 22.92 kN and 10.16, 15.13, 19.85 kN respectively. Flow value before and after conditioning of sample was found to be 3.29, 3.35, 3.40 and 3.66 mm, 3.30, 3.34 mm respectively. After observing Marshall Strength and flow value before and after conditioning of the samples, Retained Marshall Stability percentage was calculated. It has been found that Retained Marshall Stability percentage for CRDS-4 was better (86 %) than CRDS-1 (76 %) and neat bitumen (68 %).

5.3.3.2 RUTTING RESISTANCE TEST

The rutting resistance test was performed according to (EN12697–22:2003+A1) described in chapter 3 by the wheel tracking apparatus. As per this method, prepared mix slab with dimension (300 × 300 × 40) mm was tested in Wheel Tracing apparatus to observe the rutting. During the test period, rut depth was measured at different cycles rutting depth after 10,000 cycles was found to be 6.18, 2.92 and 2.24 mm for neat bitumen, CRDS-1 and CRDS-4 respectively (Figure 5.8). The rut depth values at different cycles were given in Figure 5.9. These data indicate that the higher rutting resistance of CRDS-4 and hence better performance over CRDS-1 and neat bitumen.

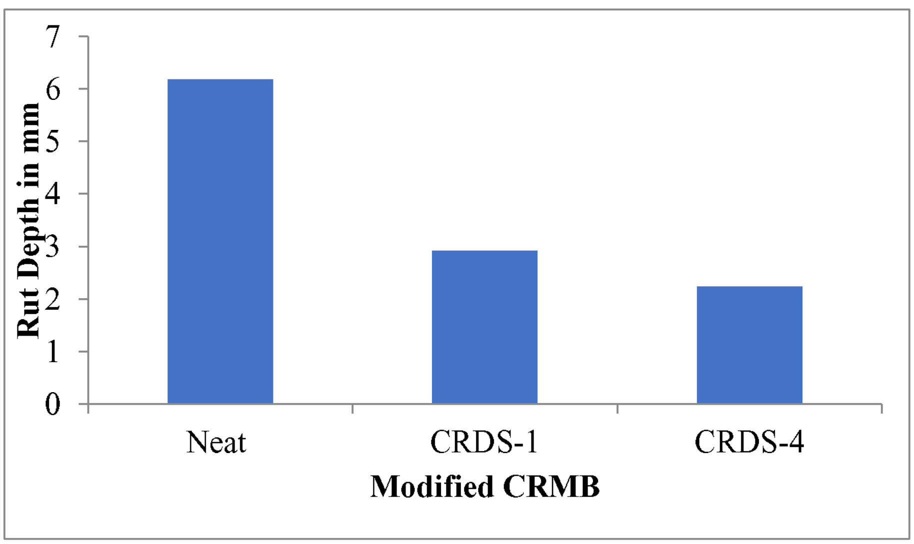

Figure 5.8: Rut depth different CRMB blends

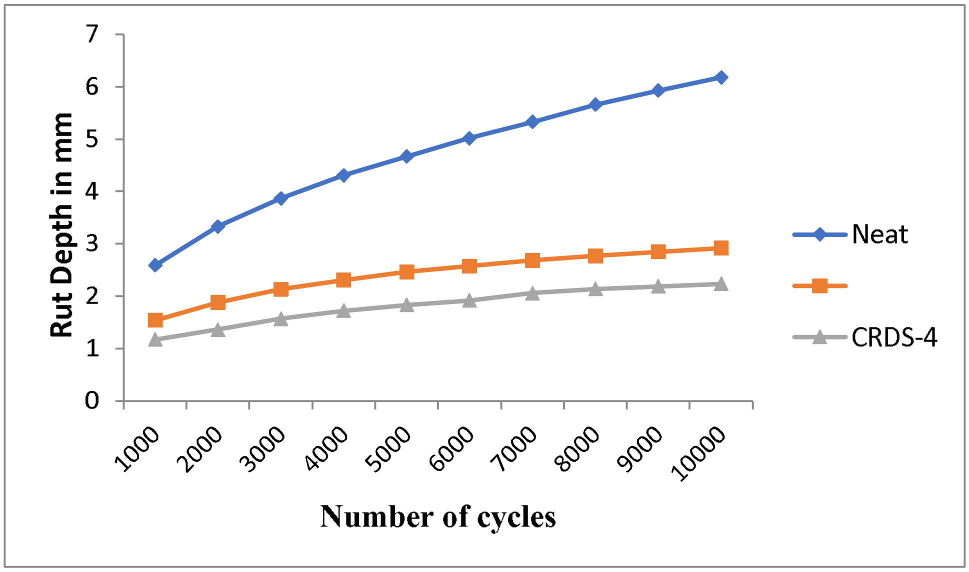

Figure 5.9: Rut depth of CRMB blends at different cycle

5.4 CONCLUSION

These studies have demonstrated a safer way of crumb rubber disposal by bituminous road pavement. Thus, seven different ratios of DETA and stearic acid, i.e. 1:0, 0:1, 1:1, 1:2, 1:3, 2:1 and 3:1 were prepared for bitumen modification to improve the stability of CRMB. The result showed that addition of DETA and stearic acid additives in combination were found to promote anchoring of crumb rubber modified bitumen. We have found that, CRDS-4 blend with 1:1 ratio of DETA and stearic acid, was much more pronounced to enhance the storage stability (2.4 °C) as compare to other prepared blends. The results from the above study were concluded below:

- Storage stability of CRDS-4 (Bitumen + CR + DETA 0.3% + stearic acid 0.3%) was highest as compared to rest other prepared crumb rubber modified bitumen blends.
- The DSR result showed that the rotational viscosity of prepared CRMB blends were decreased gradually with addition of DETA and stearic acid as comparison to CRDS-1 (reference sample) without hampering in the penetration and softening point of all the prepared blends.

- According to BBR results, CRDS-4 blend was found to have better rutting resistance of binder as compared to rest others. CRDS-4 was found to have highest value for G*/Sinδ 1.19 kPa for unaged and 2.35 kPa for RTFO aged binder as compared to others and neat bitumen. Prepared CRDS-4 blend was found to have best rutting factor and hence possess highest rutting resistance.
- From BBR test, CRDS-4 was found to have significant stiffness values (173 MPa) and m-values (0.331) at 331 at -18 °C compared CRDS-1, i.e. 243 MPa, 0.281 respectively, which resulted that CRDS-4 meet the creep stiffness specification up to -18 °C, thereby meet the performance for -28 °C in term of creep stiffness.
- The MSCR test data obtained (Jnr difference and % Recovery) after multiple stress creep recovery test showed that the prepared CRDS-4 blend sample will be good even for extremely heavy traffic road condition.
- Retained Marshall Stability percentage of CRDS-4 (86%) mix was better than CRDS-1 (76%) and neat bitumen (68%).
- Rutting depth was found to be 6.18, 2.92 and 2.24 mm for neat bitumen, CRDS-1 mix and CRDS-4 mix respectively. These data indicate that the higher rutting resistance of CRDS-4 and hence its better performance over CRDS-1 and neat bitumen.