# CHAPTER 6

# IMPROVEMENT OF STORAGE STABILITY AND RHEOLOGICAL PROPERTIES OF CRUMB RUBBER MODIFIED BITUMEN USING WASTE PET DERIVATIVE WITH DIOIC ACID

*Waste tires and PET bottles are globally largest stream of solid waste and are major environmental concern due to landfills. Hence, in this study, we have demonstrated a cleaner and novel way to reduce this environment hazards by utilizing the crumb rubber derived from waste tires and synthesized PET derivatives for enhancement of storage stability of crumb rubber modified bitumen (CRMB) along with dioic acid with bitumen modification for road pavement and sustainable development. In this study, we have prepared several modified CRMB blends (CRMB-1 to CRMB-10) and investigated the storage stability along with all physical properties of modified blends. With that we have also performed the rheological properties like DSR, BBR MSCR tests of the prepared blends and compared with conventional CRMB. Furthermore, performance properties like retained Marshall Stability and rut depth of desired blends has also been carried out.*

## 6.1 INTRODUCTION

Polyethylene terephthalate (PET) is non-biodegradable thermoplastic polyester used as a packaging material and remains in environment for a longer period. According to a report published by European Commission, the global plastics production was 245 Mt in 2008, which further reduced to 230 Mt in 2009, out of which 40% of world production was contributed by EU and China alone.[111]

Worldwide plastic has increased drastically from 2006 to 2014, due to long durability (Figure 6.1). According to a report published (Plastics Europe et al., 2015)[112] on average, 25 MT of plastic waste is generated in Europe per year. It showed, out of 25 MT, i.e. 29.7% of waste plastic was effectively recycled and 39.5% was sent to energy recovery. With that the remaining 30.8% portion was accounted for landfill, which create an environmental hazard. Figure 6.2 showed that a decrease of landfill up to 38%, while an increase in energy recovery 46% and recycling 64%.

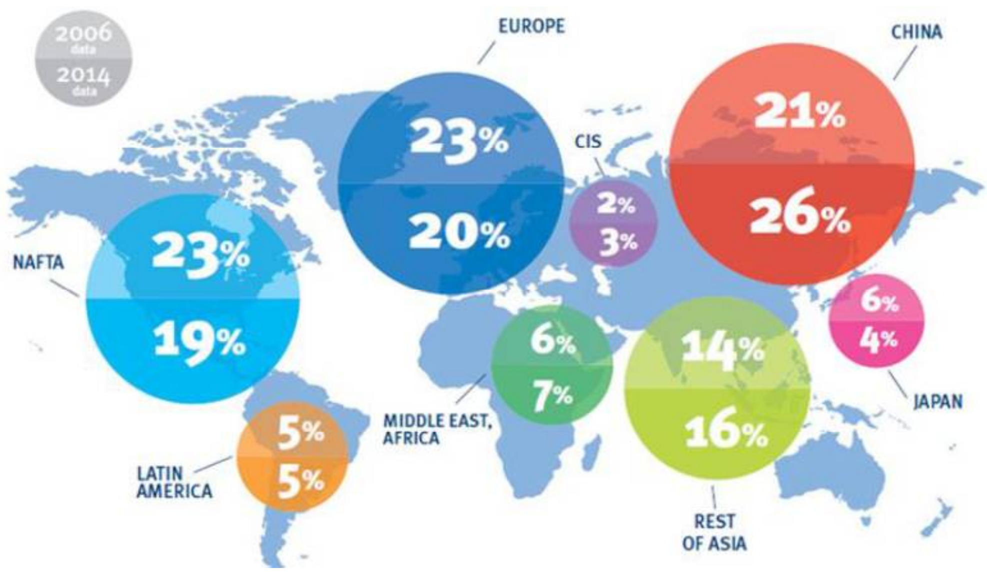


Figure 6.1: World waste plastic production 2006-1014 (Plastics Europe et al., 2015)

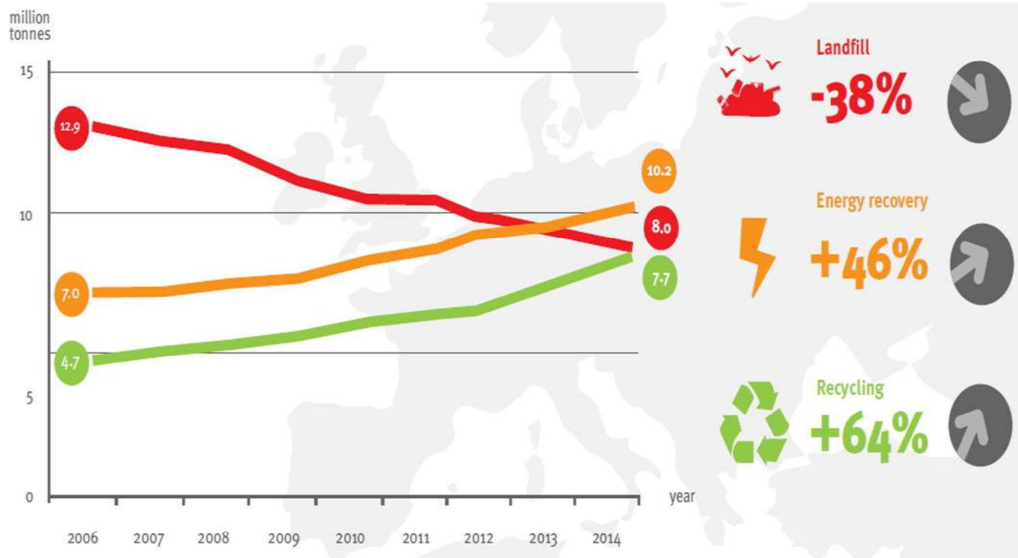


Figure 6.2 Disposal Fraction of waste plastic via landfill, recycling and energy recovery (Plastics Europe et al., 2015)

Thus, the recycling of waste PET is only the way for addressing the problem of disposal for potential environmental and economic benefits. The waste PET products are excellent candidates for thermal recycling. Plastic manufacturers do not want to invest substantial resources in new capital equipment to produce new PET polymer material. Existing recycling facilities are not sufficient to process the huge amounts of waste generated. There are major incentives from environmental perspectives and governmental regulatory directives to find new and improved uses for waste PET.

Another waste material is the crumb rubber derived from automotive and truck scrap tires. Generally, 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 conservation of natural resources but also able to create a high-performing bitumen pavement in comparison with conventional paving grade bitumen. It also deals with an environmental solution for the disposal of scrap tires.[98] According to researchers there is an increasing the performance grade (PG) of the bitumen by adding of CR to bitumen. This improves the high temperature rutting resistance and low temperature cracking.[99-103]

There are two processes (wet process and dry process) for the production of crumb rubber modified bitumen, in which the wet process is very well known.[3] Various researchers suggested that crumb rubber modified bitumen obtained through the wet process has lower fatigue, reflective cracking and greater resistance to rutting. [3, 113-117] Bitumen-rubber pavement has lower maintenance costs,[4] lower noise generation, [104-106] higher skid resistance.[107]

One of the major issues of such method is the possibility of production of a non-homogeneous blend and a phase separation occurs between the crumb rubber particles and the binder during the storage and transportation of CRMB without agitation. Due to this phase separation, most of the crumb rubber particles are settled down at the bottom of the container. Sometimes emigration of crumb rubber particles to the top of the storage vessel has also occurred. This type of different mechanisms creates an unstable condition in a rubberized bitumen blend with varied properties. [8-11, 80] The variation in storage stability between different modified binders is due to the variation in crumb rubber modifier compositions. [81-83]

To sort out this problem, researchers have modified the chemical bonds between the modifying agent and bituminous compound.[118-120] 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] 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 permanent deformation and thermal cracking resistance with improved storage stability of CRMB. Therefore, both waste PET and crumb rubber has drawn attention of worldwide scientists for safe, cheap and economic way for disposal.

In the current research, we have used a novel approach of disposable of crumb rubber and waste PET in bitumen modification for economic importance. Keeping all these issues in mind regarding waste materials and storage stability of CRMB, we have evaluated the synergic effect of synthesized waste PET derivative and sebacic acid in term of enhancement of storage stability with improvement of rheological and performance properties of CRMB.

## 6.2 RESEARCH METHODOLOGY

### 6.2.1 MATERIALS

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

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

Polyethylene terephthalate (PET) were obtained from waste plastic water bottles from garbage, which was shredded into small flakes of the size of 5-10 mm. Shredded flakes were cleaned thoroughly with water and dried flakes were stored in glass beaker at room temperature.

Sebacic acid (purity >98%) was obtained from Sigma-Aldrich (India) and used without any further purification.

### 6.2.2 METHODS

#### 6.2.2.1 PREPARATION OF PET DERIVATIVE BY AMINOLYSIS

The preparation of PET Derivative is shown in Figure 6.3. A round bottom flask was taken and filled with 30 grams of waste PET (in the form of small flakes), 100 ml xylene, and 60 grams of a polyamines e.g. diethylenetriamine (DETA), triethylenetetramines (TETA) and tetraethylenepentamine (TEPA). Then flask was placed in a heating mantle and is heated at 140 to 150 °C to reflux up to the solution turned consistent. After that the unreacted amine or other by-products were recovered. Then, the required product was taken for bitumen modification.[121]

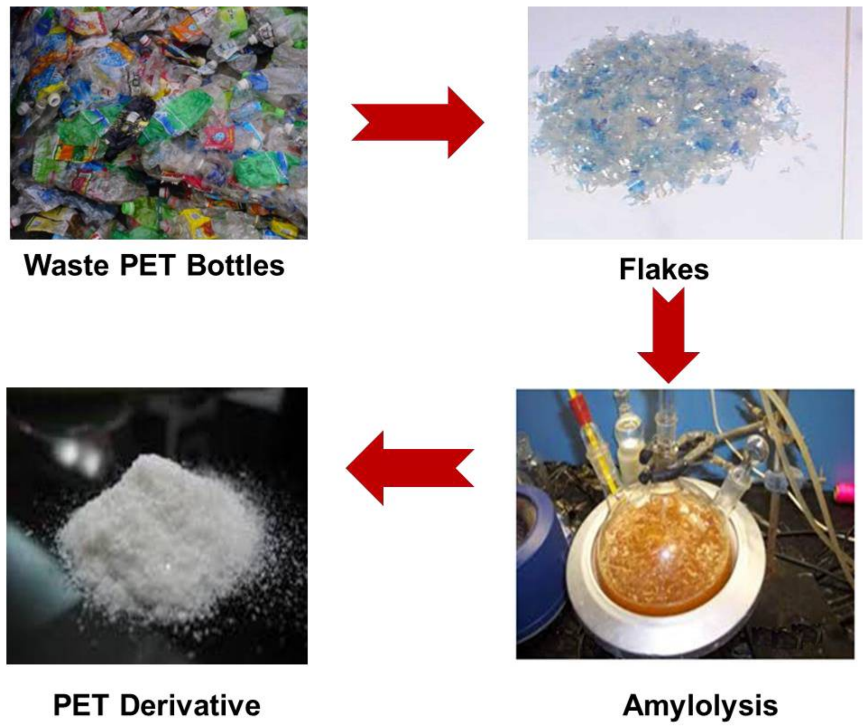


Figure 6.3: Preparation of PET Derivative

The chemical reaction of waste PET with polyamine is given in Figure 6.4.

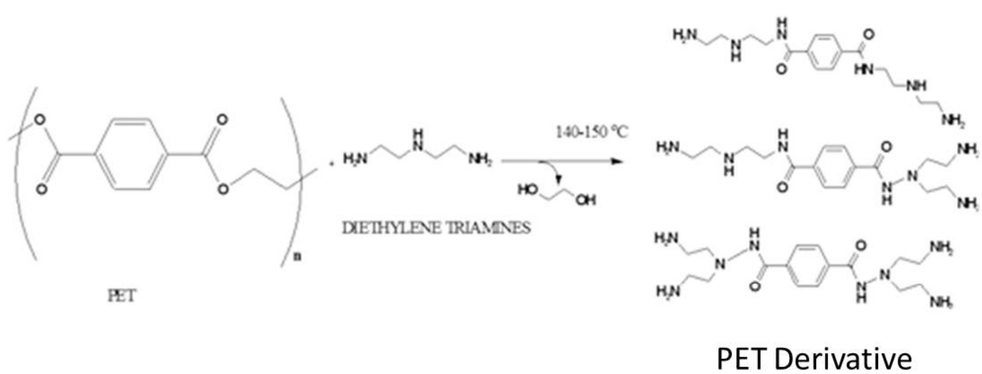


Figure 6.4: Chemical conversion of PET to PET Derivative

#### 6.2.2.2 PREPARATION OF CRMB BLENDS

In this modification process, there is a combination of bitumen, crumb rubber (CR), synthesized waste PET derivative and sebacic acid. VG-10 grade bitumen was blended with

10% crumb rubber at 160-170 °C for one hour using conventional mixer to form CRMB-1. After that 0.5% sebacic acid was added to CRMB-1 and blended for one hour at the same temperature to produce CRMB-2. Likewise, 1% and 2% of sebacic acid were added to CRMB-1 to form CRMB-2A and CRMB-2B. Similarly, 0.5%, 1% and 2% of synthesized PET derivatives were added to CRMB-1 and blended for one hour to form CRMB-3, CRMB-4 and CRMB-5 respectively. Then 0.5% of sebacic acid was further added to CRMB-3, CRMB-4 and CRMB-5 and blended for one hour to form CRMB-6, CRMB-7 and CRMB-8 as summarized in Table 6.3. Furthermore, 1% and 2% of sebacic acid were added to CRMB-3 and blended for one hour to form CRMB-9 and CRMB-10.

## 6.3 RESULTS AND DISCUSSION

### 6.3.1 PHYSICAL PROPERTIES

The physical properties of CRMB including penetration at 25 °C, softening point, elastic recovery at 15 °C and viscosity at 150 °C were tested in accordance with their ASTM standards. The neat bitumen and prepared blends viz: CRMB-1, CRMB-2, CRMB-2A, CRMB-2B CRMB-3, CRMB-4, CRMB-5, CRMB-6, CRMB-7, CRMB-8, CRMB-9 and CRMB-10 blends were taken for conventional tests like penetration, softening point, elastic recovery and viscosity and separation test. All the tests were carried out as per ASTM test method and the test results are given in Table 6.1.

Table 6.1 summarized the physical properties of modified bitumen such as penetration value, softening point, elastic recovery, viscosity and separation test.

We have found that penetration depth ranged from 25 to 86 dmm, CRMB-2A and CRMB-2B have lowest penetration, i.e. 33 and 25 dmm, which was decreased from neat bitumen, i.e. 86 dmm respectively. However, penetration of other CRMB blends was found to comparable to CRMB-1. Similarly, softening point of modified CRMB have increased from neat bitumen and ranged from 46 to 80 ºC. Softening points of CRMB-2A and CRMB-2B was found to be highest, i.e. 70 and 80 ºC, however, the separation value CRMB-7 was found to be the lowest one, i.e. 1.9 ºC compare to CRMB-2A and CRMB-2B, i.e. 5 ºC respectively. Elastic recovery (ER) of modified bitumen blends were found to be increased from neat, i.e. 15%. Table 6.1 showed that elastic recovery of CRMB-2A and CRMB-2B were lower compared to CRMB-1, however, other blends were found to be close to 71±1% . It is cleared from Table 6.1, that the rotational viscosities of all modified bitumen at 150 °C decreases in comparison to CRMB-1. Incorporation of PET derivatives along with sebacic 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.

Table 6.1 Physical properties of modified bitumen

| Sample code | % of VG-10 | % of CR | % of PET Derivative | % of Sebacic acid | Penetration In dmm | Softening Point in °C | ER@ 15 °C in % | Viscosity@ 150°C in Poise | Separation value in °C |
|---|---|---|---|---|---|---|---|---|---|
| Neat | 100 | - | - | - | 86 | 46 | 15 | 1.63 | - |
| CRMB-1 | 90.0 | 10 | - | - | 47 | 56 | 70 | 6.80 | 8.0 |
| CRMB-2 | 89.5 | 10 | - | 0.5 | 51 | 58 | 72 | 6.65 | 3.4 |
| CRMB-2A | 89.0 | 10 | - | 1.0 | 33 | 70 | 58 | 4.22 | 5.0 |
| CRMB-2B | 88.0 | 10 | - | 2.0 | 25 | 80 | 58 | 3.75 | 5.0 |
| CRMB-3 | 89.5 | 10 | 0.5 | - | 50 | 57 | 71 | 6.67 | 5.0 |
| CRMB-4 | 89.0 | 10 | 1.0 | - | 51 | 57 | 72 | 6.50 | 3.4 |
| CRMB-5 | 88.0 | 10 | 2.0 | - | 49 | 57 | 72 | 6.20 | 3.6 |
| CRMB-6 | 89.0 | 10 | 0.5 | 0.5 | 52 | 56 | 71 | 6.15 | 2.8 |
| CRMB-7 | 88.5 | 10 | 1.0 | 0.5 | 52 | 57 | 72 | 6.18 | 1.9 |
| CRMB-8 | 87.5 | 10 | 2.0 | 0.5 | 52 | 56 | 70 | 6.15 | 2.6 |
| CRMB-9 | 88.5 | 10 | 0.5 | 1.0 | 50 | 57 | 72 | 5.41 | 6.0 |
| CRMB-10 | 87.5 | 10 | 0.5 | 2.0 | 50 | 57 | 72 | 5.32 | 7.5 |

### 6.3.1.1 STORAGE STABILITY TEST

Storage stability test data for all the prepared blends are given in Figure 6.5.

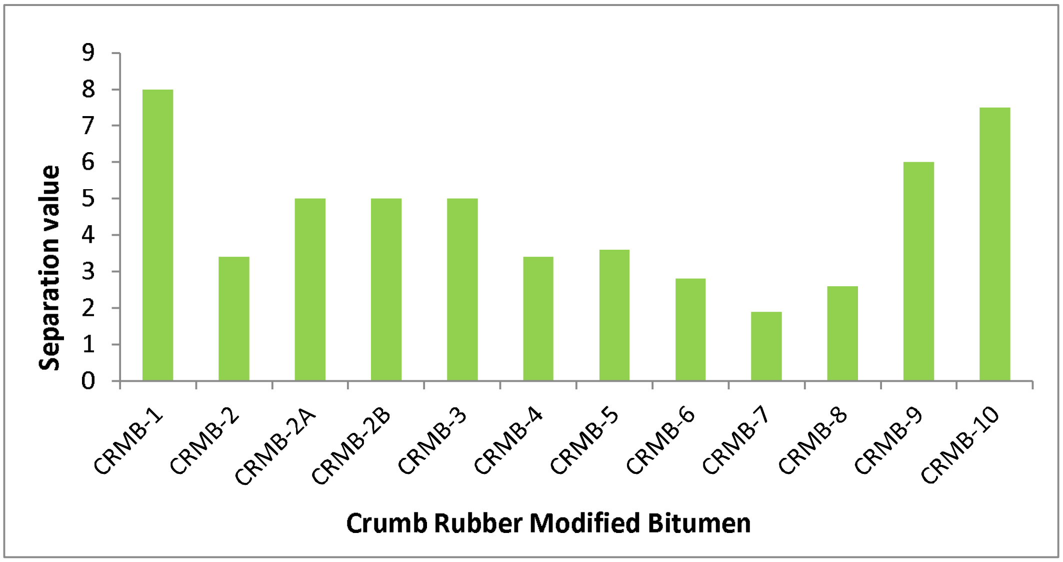


Figure 6.5: Separation value of all CRMB blends

It showed the separation value of different CRMB blends, which ranged from 1.9 to 8.0 ºC. It showed that with increased sebacic acid concentration from 0.5 to 1.0 and 2.0% (CRMB-2, CRMB-2A and CRMB-2B), we have found that separation value was increased from 3.4 to 5.0 ºC respectively. This may be due to hardening of bitumen which reflects in term of increase in softening point with reduced elasticity. Separation value of CRMB-7 was found to be minimum, i.e. 1.9 ºC as compared to reference blend CRMB-1 (8.0 ºC) and rest of other blends, which was attributed due to lengthening of amide chain, in-situ formed with addition of PET derivative and sebacic acid inside the body of bitumen. The result showed that separation value was decreased from 8.0 to 5.0, 3.4 and 3.6 ºC with increased conc. of waste PET derivative from 0 to 0.5, 1.0 and 2.0% for CRMB-1, CRMB-3, CRMB-4 and CRMB-5 respectively.

However, in combination keeping sebacic acid conc. to 0.5%, the separation value was decreased from 2.8 to 1.9 ºC for CRMB-6 and CRMB-7 respectively. Further increased in waste PET conc. from 1.0 to 2.0% has not significantly reduce the separation value. We have demonstrated the synergic effect of waste PET addition with increase conc. of sebacic acid from 1.0 to 2.0%, which increased the separation value from 6.0 and 7.5 °C respectively. That may be explained due to excess amount of sebacic acid present in bituminous mixture, which was separated due to its higher density (1.21g/$cm^3$) than bitumen (1.03 g/$cm^3$).

### 6.3.2 RHEOLOGICAL PROPERTIES

#### 6.3.2.1 DYNAMIC SHEAR RHEOMETER (DSR)

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 CRMB blends are shown in Figure 6.6 and RTFO aged CRMB blends are shown in Figure 6.7. All the prepared CRMB blends doped with synthesized PET derivative and sebacic acid show an increase in $G^*/\sin\delta$ value as compared to the neat bitumen and CRMB-1 blend.

The $G^*/\sin\delta$ value at 82 °C, of unaged samples of neat bitumen, CRMB-1 and CRMB-7 were found to have 0.18, 0.75 and 1.20 kPa respectively which shows acceptable value only for CRMB-7 as per AASHTO T315-10 test method. Similarly, $G^*/\sin\delta$ value at 82 °C for RTFO aged samples of neat bitumen, CRMB-1 and CRMB-7 were found to have 0.45, 1.45 and 2.25 kPa respectively which shows acceptable value only for CRMB-7 as per AASHTO T315-10 test method. This shows that CRMB-7 blend has better high temperature rutting resistance properties as compared to CRMB-1 and neat bitumen.

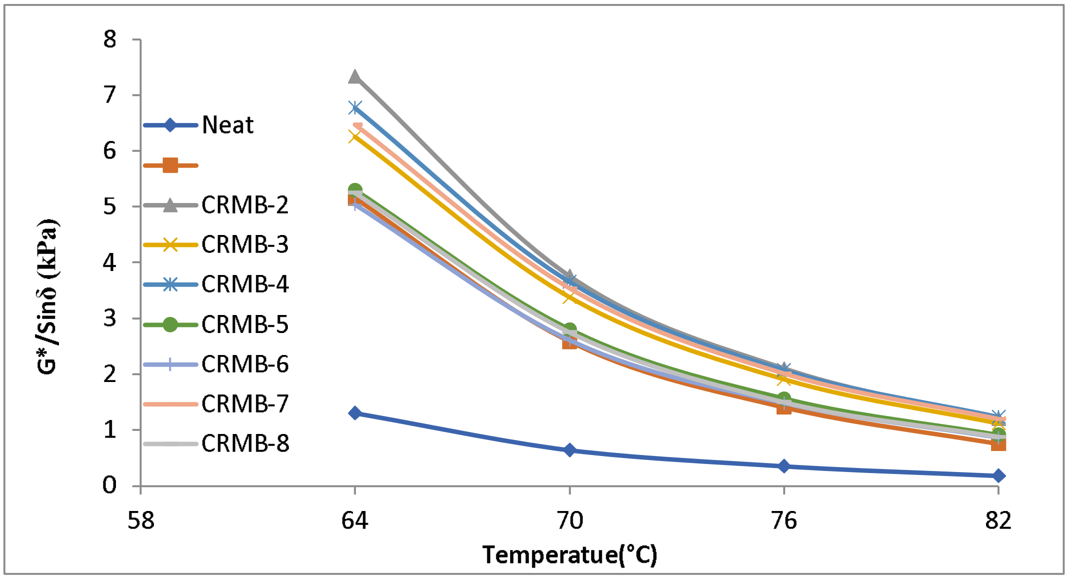


Figure 6.6: G*/Sinδ value of Unaged CRMB blends at different temp

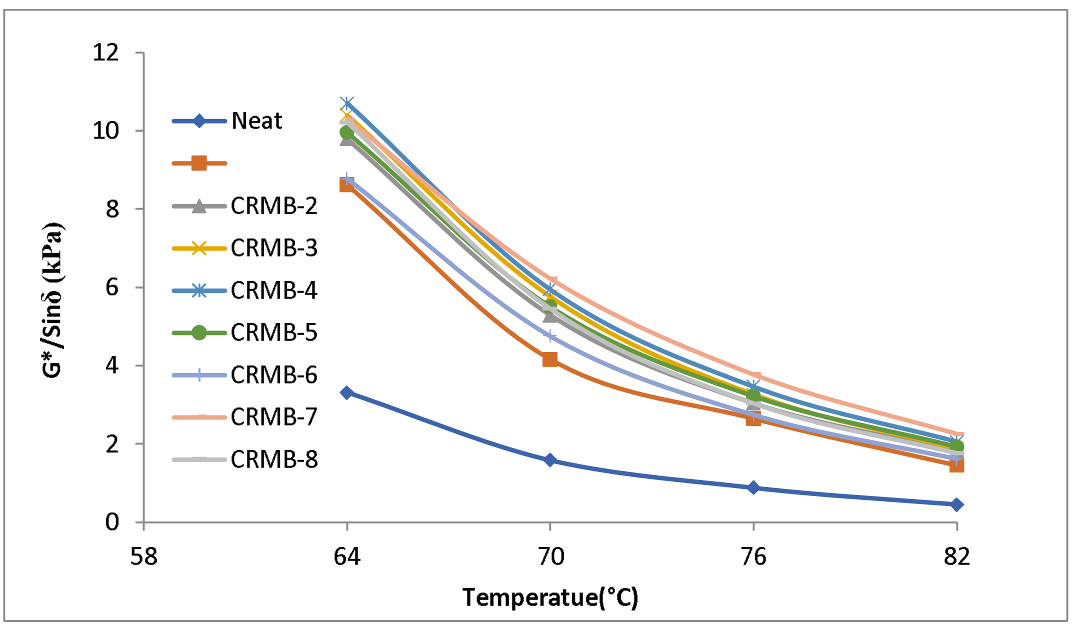


Figure 6.7: G*/Sinδ value of RTFO aged CRMB blends at different temp

#### 6.3.2.2 BENDING BEAM RHEOMETER (BBR)

The low temperature stiffness and relaxation properties 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 at -18 °C temperature for neat bitumen, CRMB-1 and CRMB-7 blends were found to be 301, 243 and 184 MPa which are less than 300 MPa except neat, to be required for passing the sample as per AASHTO T313-10 test method (Figure 6.8). Test data shows that CRMB-7 has better low temperature thermal cracking resistance as compared to CRMB-1 and neat bitumen. The m-value for neat bitumen, CRMB-1, and CRMB-7 blends at -18 °C temperature were found to be 0.279, 0.281 and 0.321MPa which shows only m-value of CRMB-7 has more than 0.3 MPa to be required for passing the sample as per AASHTO T313-10 test method (Figure 6.9).

The blend CRMB-7 was found to have best stiffness value and m-value at different temperature as compared to rest other blends as well as neat bitumen, which shows that CRMB-7 has good low temperature thermal cracking resistance. The test data also shows that even after hardening the sample was passed at very low temperature which shows a good indication of low temperature thermal cracking resistance of prepared blends in this work

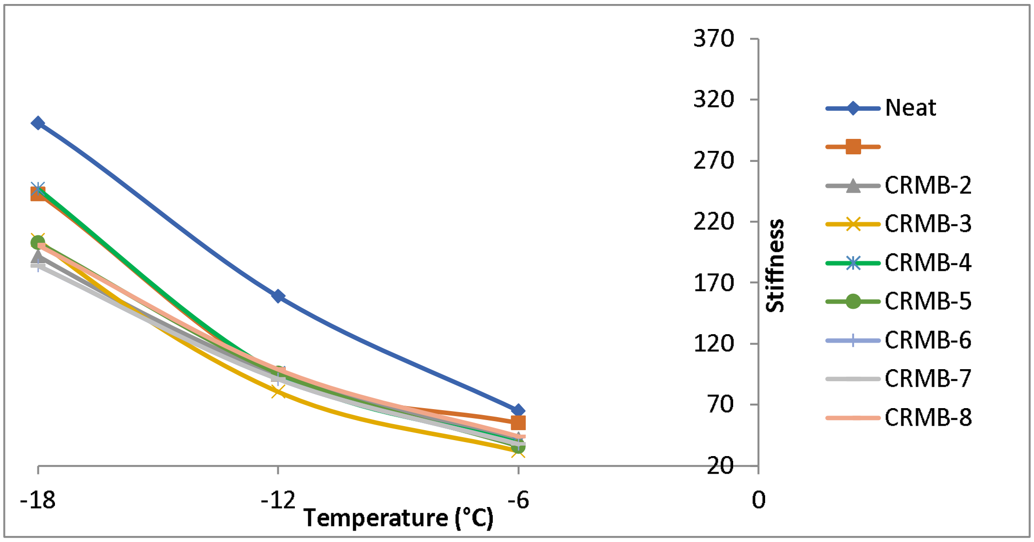


Figure 6.8: Stiffness value of CRMB blends at different temp

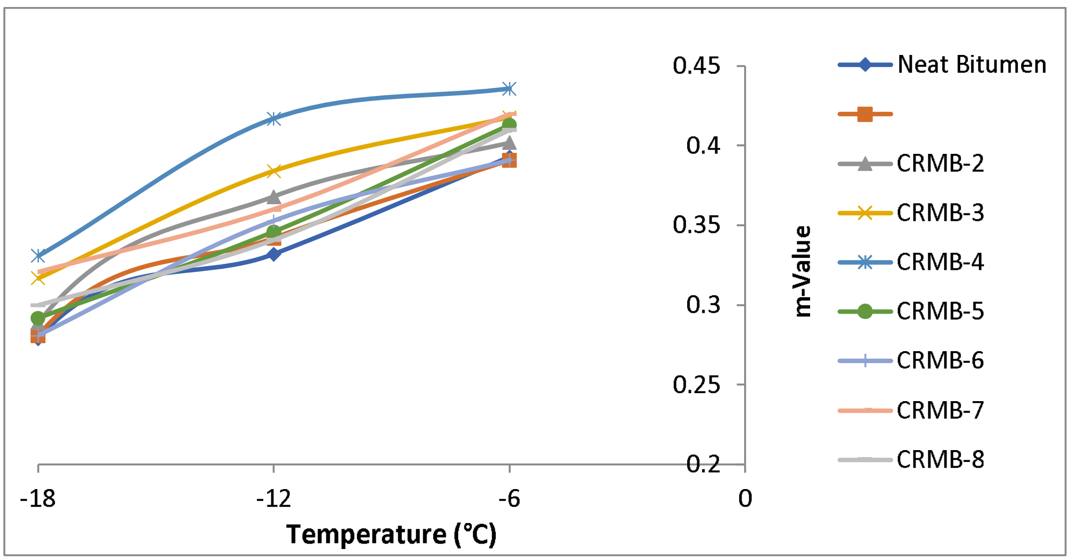


Figure 6.9: m-value of CRMB blends at different temp.

### 6.3.2.3 MULTIPLE STRESS CREEP RECOVERY (MSCR)

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.

Average percentage recovery values for CRMB-7 were also found to be greater than neat bitumen and CRMB-1 at both 0.1 and 3.2 kPa stress level (Figure 6.10). Non-recoverable creep compliance (Jnr) values at 3.2 kPa for neat bitumen, CRMB-1 and CRMB-7 blends were coming out to be 3.44, 0.52 and 0.48 which are less than 0.5 only in case of CRMB-7 blend required as per AASHTO MP19-10 specification (Figure 6.11). The obtained Jnr value for prepared blends shows that the doped sample was acceptable even at extremely heavy traffic road condition.

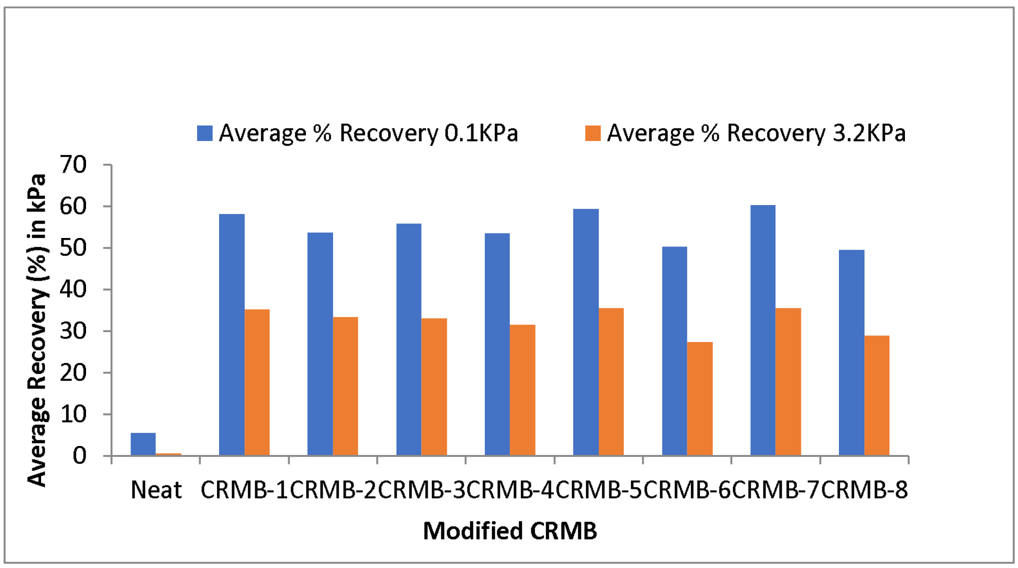


Figure 6.10: Average recovery value of CRMB blends at 0.1 and 3.2 KPa

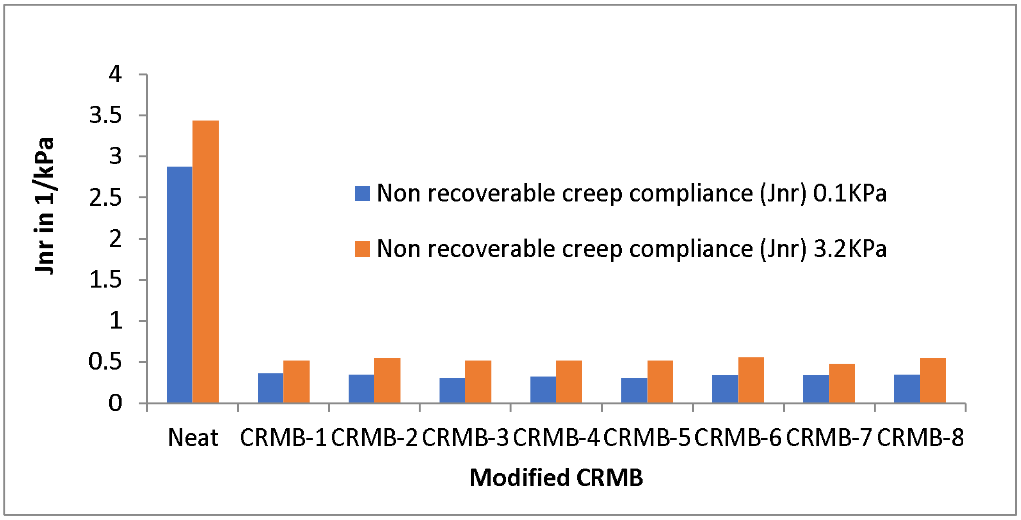


Figure 6.11: Jnr value of CRMB blends at 0.1 and 3.2 KPa

### 6.3.3 PERFORMANCE PROPERTIES

#### 6.3.3.1 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. In this test, specimen is immersed in a water bath having temperature of 60 ± 1°C for a period of 30 minutes called (before conditioning, S1) and when the same is for 24 hours then it is called (after conditioning, S2). After that specimen samples were tested in Marshall apparatus to determine the Marshall Stability and flow value of the specimen.

CRMB-7 is 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 other blends. Therefore CRMB-7 sample was investigated for Marshall Stability test and test data was compared with CRMB-1 and neat bitumen given in Table 6.2.

Table 6.2 Marshall Stability of CRMB blends

| 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 | 14.84 | 3.29 | 10.16 | 3.66 | 68 |
| CRMB-1 | 19.76 | 3.35 | 15.13 | 3.30 | 76 |
| CRMB-7 | 23.32 | 3.40 | 20.15 | 3.34 | 86 |

Marshall Strength of neat bitumen, CRMB-1, CRMB-7 before conditioning was found to be 14.84, 19.76, 23.32 kN and after conditioning was found out to be 10.16, 15.13, 20.15 kN respectively (Table 6.2). Flow value before and after conditioning of sample was found to be 3.29, 3.35, 3.40 and 3.66, 3.30, and 3.34 mm respectively. After observing Marshall Strength and flow value before and after conditioning of the samples, it has been observed that percentage of Retained Marshall Stability for CRMB-7 was better (86%) than CRMB-1 (76%) and neat bitumen (68%).

### 6.3.3.2 RUTTING RESISTANCE TEST

The rutting resistance test was performed according to the wheel tracking test method (EN12697–22:2003+A1) described in chapter 3. As per this method, prepared mix slab with dimension (300 × 300 × 40) mm was tested in Wheel Tracing apparatus to observe the rutting. Since all the physical and rheological properties of CRMB-7 blend was better as compared to rest others therefore CRMB-7 sample was further investigated for rutting test and test data was compared with CRMB-1 and neat bitumen. Rutting depth was found to be 6.18, 2.92 and 2.11 mm for neat bitumen, CRMB-1 and CRMB-7 respectively (Figure 6.12). Rutting depth for these samples at different cycle has also been observed (Figure 6.13). These data indicate the higher rutting resistance and better performance of CRMB-7 over CRMB-1 and neat bitumen.

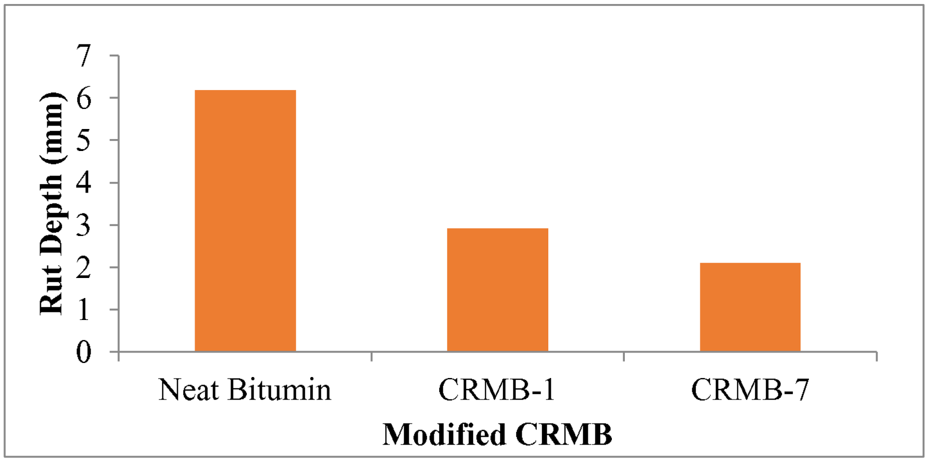


Figure 6.12 Rut Depth of different CRMB blends

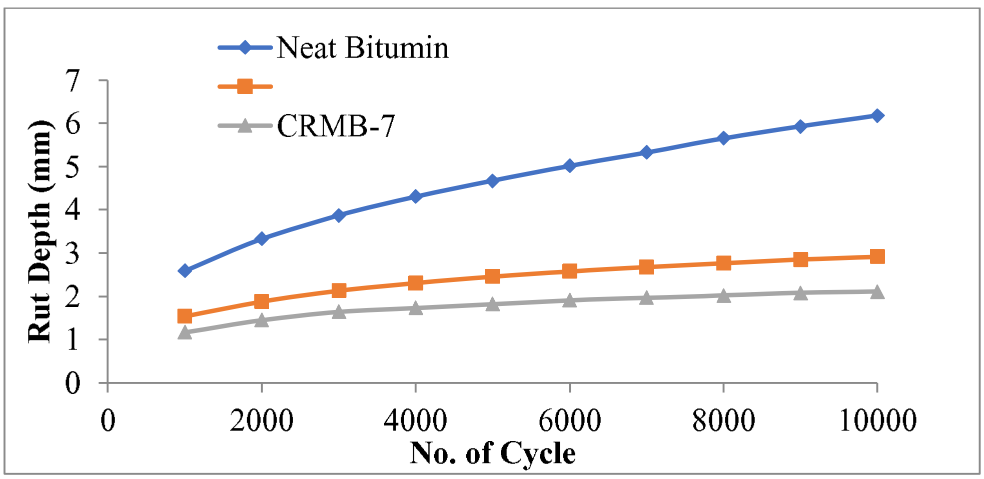


Figure 6.13: Rut Depth of CRMB blends at different cycles

## 6.4 CONCLUSION

In this work, synergic effect of synthesized PET derivatives and sebacic acid on the storage stability of crumb rubber modified bitumen has been studied. Three different combinations of synthesized PET derivatives and sebacic acid were used to observe the effect of both additives on the storage stability of CRMB (Crumb rubber modified bitumen). All the combination of synthesized PET derivatives and sebacic acid was found to promote anchoring of crumb rubber modified bitumen however CRMB-7 blend was found to have better storage stability as compare to rest other prepared blends. Therefore, CRMB-7 blend was further evaluated for all performance related properties. CRMB-7 was found to be better as compared to rest others in terms of following aspects.

- All physical properties including storage stability were improved by using waste PET derivative and sebacic acid. However, CRMB-7 (bitumen + CR + PET derivative 1% + sebacic acid 0.5%) was more storage stable than other prepared blends.
- From DSR, CRMB-7 was found to have highest value for G*/Sin δ for unaged and RTFO aged binder as compared to other blends. Prepared CRMB-7 blend was also found to have best rutting factor and hence possess highest rutting resistance.
- According to BBR, CRMB-7 was found to have best stiffness values as well as m-values at different temperature as compared to rest other blends and even neat bitumen which shows that CRMB-7 will have good low temperature thermal cracking resistance as compared to other blends.
- The MSCR test data obtained (Jnr difference and % Recovery) after multiple stress creep recovery test showed that the prepared CRMB-7 sample will be good even for extremely heavy traffic road condition.
- Retained Marshall Stability percentage of CRMB-7 mix was better (86%) than CRMB-1 (76%) and neat bitumen (68%).
- Rutting depth also indicates that the higher rutting resistance of CRMB-7 (2.11 mm) in comparison to CRMB-1 (2.92 mm) and neat bitumen (6.18 mm). Lower rut depth value means higher the rutting resistance.