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Improved Storage Stability of Crumb Rubber Modified Bitumen using Long Chain Amines

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***Abstract* - With increased transportation, waste tire rubber accumulation becomes a major environmental concern. The use of crumb rubber, recycled tire rubber is considered as an additive in bitumen modification for road pavement and economic disposal or tire rubber. Although, crumb rubber modified bitumen shows excellent performance properties due to its elastic nature but meanwhile storage stability of crumb rubber modified bitumen (CRMB) is still an issue due to poor dispersion of crumb rubber particle in bitumen, which affects the performance of road pavement. Keeping these issues in mind, we have doped various long chain amines in CRMB to improve its storage stability and physical and rheological properties CRMB.**

Keywords: Bitumen, Crumb rubber, Dodecylamine, Storage stability, Rheological Properties

1. INTRODUCTION

With increased in industrialization, economic development and population the accumulation of waste materials, i.e. plastics, rubber, metals and chemicals etc. has been increased drastically in last few decades proportionally [1]. The transportation sector has increased the scrap tires worldwide and disposal of waste tires through landfill, incineration significantly deteriorate the environment [2]. Crumb rubber (CR), which is obtained from grinding the scrap tires and be incorporated in bitumen modification due to high elastic properties of crumb rubber [3-5].

Bitumen is a viscoelastic material and is used in road pavement due to its high mechanical and rheological properties [6-8]. However, with increased transportation load on road, there is a need to the strength, fatigue, rutting, and resistance to ageing and high thermal and storage stability of bitumen. In this concern, incorporation of crumb rubber in bitumen is most preferential and economic way to improve the properties of original bitumen with recycling of crumb rubber with economic and environmental benefits [9, 10].

Recently, numerous studies have conducted to improve the performance of asphalt mixtures using anti stripping additives and polymers, i.e. styrene-butadiene-styrene [11, 12]. Much of the research was focused by varying the percentage of crumb rubber in bitumen wet process or dry process [13]. In the dry process, crumb rubber is added to the aggregate before the asphalt binder is charged into the mixture. Cao (2007) [14] showed that the dry process recycling of tire rubber with bitumen could enhance the deformation, resistance and cracking properties of modified bitumen.

In the wet process, crumb rubber bitumen is pre-blended with bitumen the rubber at high temperature and specific blending conditions [15]; [16]. Navarro et al. (2004) [17] investigated that thermorheological behaviour of bitumen modified with 9 wt. % crumb tire rubber has increased the linear viscoelastic modulus and viscosity at high temperatures (Xiao et al. 2007) [18] mentioned that the addition of crumb rubber was helpful in increasing the voids in mineral aggregate in Superpave mix design and improving the rutting resistance of bitumen mixtures regardless of rubber size and type.

Additionally, the use of rubber-particle sizes less than 0.35 mm and high shear rates during manufacturing operations was highly recommended. However, it was reported that crumb rubber-modified bitumen has a low resistance to aging due to weak physical interaction between the asphalt and polymer modifiers and have very poor storage stability at high temperature (140-180 °C) [19]. This phase separation of crumb rubber modified bitumen is mainly attributed decomposition of weak interaction between bitumen and crumb rubber and production of a non-homogeneous blend depending upon the density of modifier molecule thereof settle at the bottom or at the top of container of storage tanks during storage and transportation [20]. This type of different mechanisms creates an unstable condition in a rubberized bitumen blend with varied properties [17, 19, 21-23]. The variation in storage stability between different modified binders is due to the variation in crumb rubber modifier compositions [24-26].

Some studies claim that the increase in binder viscosity cannot be accounted for only by the existence of the rubber swelling particles [27]. The swelling of crumb rubber particles is facilitated due to the absorption of aromatic oils from the bitumen [28, 29]. A substantial amount of research studies have been carried out in bitumen modification to improve the rheological and mechanical performance, i.e. higher softening point, higher elastic recovery, reduced fatigue cracking and rutting resistance [30-32]. Many bitumen researchers have worked on using different chemical additives to improve the phase separation of bitumen modified with crumb rubber [33, 34].

Further, some researchers used grafting process to improve the properties of CRMB. In this process, the surface of crumb rubber is modified by bulk polymerization of acrylic acid [35]. Shatanawi et al. (2012) [23] showed that the storage stability of CRMB can be highly improved with the addition of furfural as an activation agent in the bitumen. Xiang et al. (2009) [36] used polymeric compatibilizer containing conjugated diene which reacts as a crosslinking agent for the formation of CRMB.
Bocoum et al. (2014) [37] reported that amine-based liquid additives facilitate rubber devulcanization for bitumen modification, which might lead to enhanced rheological properties with 10-15% of bitumen binders. Amine based binders might facilitate the release of crumb rubber particles into bitumen, thus softening the overall bitumen-rubber matrix. Similarly, Hefer et al. (2006) [38] showed that amine-based liquid modifier (0.5% by weight of bitumen) may improve the chemical interaction between bitumen–aggregate interfaces might reduce the moisture damage.

However, studies on the combined effects of long chain amines and their interaction mechanisms with crumb rubber in bitumen binder are relatively limited. Therefore, the objective of the current study is to investigate the effects various long chain certain amine-based liquid additives, i.e. Dodecylamine, Hexadecylamine and Octadecylamine on the storage stability of crumb rubber modified bitumen at high temperature. The study was further enhanced to estimate the effect of long chain amine over the rheological performance of bitumen binder.

2. MATERIALS AND METHODS

2.1 Materials

VG-10 grade (viscosity grade) bitumen was obtained from Mathura Refinery; Indian Oil Corporation Ltd. (India) was used for all experimental activities. Physiochemical properties of neat bitumen were given in Table 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 2.

Long chain amine like Dodecylamine (Purity, 98 %), Hexadecylamine (Purity, 90 %) and Octadecylamine (Purity, 90 %) were obtained from Acros Organics and used without any further purification.

2.2 Bitumen Modification Method

In this modification process, there is a combination of bitumen, crumb rubber (CR) and dodecylamine (DDA). Firstly, the appropriate amount of CR was determined by optimizing the various percentages of CR (8, 10 and 12 weight percent of bitumen). Based on the results of conventional bitumen tests, the optimum amount of CR was determined as 10 % of bitumen. In this paper, we have used three different types of long chain amines like hexadecyl amine, octadecyl amine and dodecyl amine for CRMB modification. Initially, we have taken 0.5 % of all three amines separately for CRMB modification. Among all three long chain amines modified CRMB blend, the storage stability of DDA doped CRMB was found to be good as compared to rest others. Therefore, the amount of DDA was further optimized by taking four different percentages (0.1, 0.3, 0.5 and 0.7 weight percent of bitumen). VG-10 grade bitumen was blended with 10% CR at 160-170 °C for one hour using a conventional mixer to form CRDDA-1. After that 0.1-0.7 %, DDA was added to CRDDA-1 and blended for one hour at the same temperature to produce CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5.

3. RESULTS AND DISCUSSION

3.1 Physical Properties

The neat bitumen and prepared blends: CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 blends were characterized their physical properties like penetration at 25 °C, softening point and elastic recovery at 15 °C and viscosity at 150 °C according to ASTM D5, ASTM D36, ASTM D6084 and ASTM D4402 respectively The results of these tests are given in Table-3.

The results showed that all the developed formulations were found to have decrease in penetration, viscosity, separation value and increase in softening point, elastic recovery as compared to reference sample CRDDA-1.

3.1.1 Storage Stability Test

The Storage stability test is a method to check the separation of CRMB's under storage. It is characterized according to ASTM D7173. In this test, samples are put in an aluminium tube and heated at 163 °C for 48 hours without disturbance. After that, the sample was placed in the freezer for 4 hours to solidify CRMB. Then the tube was removed from the freezer and cut into three equal parts by spatula and hammer. The softening points of top and bottom part of the sample were tested separately. Then the difference in softening points between the top and the bottom part of the tube was measured in °C. Lower the separation value higher is the storage stability of modified blends.

The test results indicate that increase in percentage of DDA the separation value of the modified blend decreases initially but further addition of DDA in CRMB again enhance the separation value (Figure-1). Out of several prepared blends 0.3% and 0.5% DDA doped CRMB blends i.e. CRDDA-3 (separation value 3.8 °C) and CRDDA-4 (separation value 3.6 °C) were found to have better storage stability as compared to reference sample CRDDA-1 (separation value 8.0 °C) and meeting requirement of separation value less than 4 °C as per CRMB specification (IS 15462: 2004).

Crumb rubber modified bitumen doped with long chain amine produces a remarkable improvement on the storage stability. Crumb rubber particles get absorbed in the oil portion of bitumen causing increasing viscosity of modified blend. Incorporation of long chain amines in the crumb rubber modified bitumen may increase the oil portion of bitumen which further enhances physical absorption of crumb rubber particles and leads to improve storage stability of modified blends. Crumb rubber particles may chemically have anchored with long chain amine inside the bituminous matrix which also improves storage stability. Storage stability of CRMB blends increased when amount of DDA increases from 0.1-0.5 %. But further addition of DDA (0.7 %) in CRMB blend unexpectedly decreases the storage stability of prepared blend. This is because, when all the reacting moiety present in bituminous mixture react with doped DDA molecules then excess amount of DDA molecules migrate at the top of the container due to its lower density (0.80 g/cm^3) than bitumen (1.03 g/cm^3) and separation occured.

3.2 Rheological Properties

3.2.1 Dynamic Shear Rheometer (DSR) Test

All the DSR testing was performed on Anton Par MCR102 by using the method AASHTO T315-10. The behavior of all unaged modified bitumen is shown in Figure 2 and the RTFO (Rolling Thin Film Oven) aged modified bitumen is shown in Figure 3.

The G*/Sinδ value of all prepared blends (unaged) i.e. CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 are 0.75, 0.84, 1.07, 1.02 and 1.01. However, G*/Sinδ value of CRDDA-3, CRDDA-4 and CRDDA-5 were found to be acceptable at 82 °C as per AASHTO T315-10 (G*/Sinδ ≥ 1 kPa).

The G*/Sinδ value of all prepared blends (RTFO-aged) i.e. CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 are 1.45, 1.74, 1.83, 2.43 and 1.79. In case of RTFO aged samples, only CRDDA-4 was found to have acceptable value for G*/Sinδ at 82°C as per AASHTO T315-10 (G*/Sinδ ≥ 2.2 kPa). From the above aged and unaged G*/Sinδ values, it has been observed that only CRDDA-4 blend possess good rutting and fatigue factor as compared to other prepared blends.

3.2.2 Bending Beam Rheometer (BBR) Test

The Bending Beam Rheometer (BBR) test provides a measure of low temperature stiffness and relaxation properties of asphalt binders. These parameters give an indication of an asphalt binder's ability to resist low temperature cracking. All tests were performed in Cannon BBR Instrument.

The stiffness value at -18 °C for CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 blends are 243, 239, 231, 163 and 203 MPa respectively. All stiffness values are less than 300 MPa to be required for passing the sample as per AASHTO T313-10 (Figure 4).

The m-values at -12 °C for CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 blends are 0.342, 0.331, 0.317, 0.316 and 0.359 respectively. All m-values were found to be greater than 0.3 to be required for passing the sample as per AASHTO T313-10 test method (Figure 5). From the above stiffness values, it has been observed that CRDDA-4 has lowest stiffness value (163 MPa). All the Dodecylamine doped CRMB blends will have good low temperature thermal cracking resistance as compared neat bitumen but at par with conventional CRDDA-1.

3.2.3 Multiple Stress Creep Recovery (MSCR) Test

This test can be used to characterize recoverable strain (elastic response) and Jnr (non-recoverable creep compliance) of bitumen binders modified with polymer, more accurately than conventional DSR test.

Average percentage recovery values for CRDDA-1, CRDDA-2, CRDDA-3, CRDDA-4 and CRDDA-5 blends at 0.1 kPa are 61, 62, 65, 65 and 49 % and at 3.2 kPa 36, 36, 37, 37 and 29 % respectively (Figure 6). The average percentage recovery data showed that CRDDA-3 and CRDDA-4 have higher average percentage recovery compared to neat bitumen and other prepared blends.

Non-recoverable creep compliance (Jnr) values at 0.1 kPa for CRDDA-1, CRDDA-2 CRDDA-3, CRDDA-4 and CRDDA-5 blends were coming out to be 0.29, 0.27, 0.23, 0.23 and 0.43 kPa^{-1} respectively. Non-recoverable creep compliance (Jnr) values at 3.2 kPa for CRDDA-1, CRDDA-2 CRDDA-3, CRDDA-4 and CRDDA-5 blends were coming out to be 0.52, 0.50, 0.48, 0.45 and 0.64 kPa^{-1} respectively (Figure-7). From the above data, CRDDA-3 and CRDDA-4 have lower Non-recoverable creep compliance (Jnr) value at both 0.1 and 3.2 kPa which showed that CRDDA-3 and CRDDA-4 blends will be acceptable even at extremely heavy traffic road condition as per AASHTO MP19-10 specification (Jnr ≥ 0.5 Mpa for extremely heavy traffic road condition).

4. CONCLUSION

These studies have demonstrated a safer way of crumb rubber disposal by bituminous road pavement. The result showed that addition of Dodecylamine (DDA) in rubberized bitumen was found to promote anchoring of crumb rubber. We have found that, CRDDA-4 blend with 0.5% of DDA, was much more pronounced to enhance the storage stability (separation value decreases from 8 °C to 3.6 °C) as compare to other prepared blends. The results from the above study were concluded below**:**

1. Physical properties of DDA doped crumb rubber modified bitumen i.e. penetration, softening point, elastic recovery, viscosity and storage stability were improved by adding long chain amine (Dodecylamine).
2. From DSR test data, CRDDA-4 was found to have highest value for G*/Sinδ for unaged and for RTFO aged binder as compared to other prepared blends. Prepared CRDDA-4 blend was found to have best rutting factor and hence possess highest rutting resistance property at high temperature.
3. According to BBR results, all formulation of DDA doped crumb rubber modified bitumen showed lower stiffness and meet the acceptable criteria up to a temperature of -18 °C i.e. low temperature performance specification for -28 °C in terms of creep stiffness. However, CRDDA-4 formulation was found to have best stiffness values and m-values at different temperature as compared to rest other blends, which

shows that CRDDA-4 will have good low temperature thermal cracking resistance as compared to other blends.

4. MSCR test data revels that, Non-recoverable creep compliance (Jnr) values of all DDA doped crumb rubber modified bitumen formulations are meeting the criteria for extremely heavy traffic road condition according to AASHTO MP19-10. In addition, the prepared CRDDA-4 blend has lowest Jnr-value.
5. According to all above test results, crumb rubber modified bitumen doped with optimized amount of Dodecylamine enhances storage stability along with improvement in rheological properties.

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List of Tables

Table 1. Properties of neat bitumen

Properties	Neat Bitumen	Reference Specification
Penetration at 25 °C (100 g, 5 s) 0.1mm	86	IS:1203-1978
Softening Point, °C	46	IS:1205-1978
Absolute Viscosity (60 °C), Poise	1333	IS:1206 (PART-2)
Kinematic Viscosity (135 °C), cst	367	IS:1206 (PART-3)
Viscosity at 150 °C, Poise	1.63	ASTM:D4402
Ductility at 25°C (5 cm/min), cm	100+	IS:1208-1978
Ductility after TFOT at 25 °C, cm	100+	IS:1208-1978
Flash point open cup (COC), °C	245	IS:1209
Compositional analysis (%)		
Saturates	3.4	
Aromatics	42.9	
Resins	32.9	
Asphaltene	20.8	

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Table 2. Properties of crumb rubber

Properties	Crumb rubber	Reference Specification
Ash content	5.6%	ASTM D5667-95
Moisture content	0.51%	ASTM D5668-99
Toluene Insoluble	58.6%	-
Type of Rubber	Isoprene	IS 5650
Particle size passing through 600 µm	100%	ASTM D5667-95

Table-3: Conventional properties of different CRMB blends

Sample code	% of VG-10	% of CR	% of DDA	Penetration In dmm	Softening Point in °C	ER@ 15 °C in %	Viscosity@ 150 °C in Poise	Separation Value (°C)
Neat Bitumen	100	-	-	86	46	15	1.63	-
CRDDA-1	90	10	-	47	56	70	6.80	8.0
CRDDA-2	89.9	10	0.1	46	56	70	5.97	7.0
CRDDA-3	89.7	10	0.3	45	57	72	5.33	3.8
CRDDA-4	89.5	10	0.5	45	57	73	5.13	3.6
CRDDA-5	89.3	10	0.7	45	57	71	5.63	5.8

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Figure-2: G*/Sinδ value of Unaged blends
Figure-3: G*/Sinδ value of RTFO aged blends
Figure-4: Stiffness of CRMB blends at different Temp.
Figure-5: m-value of CRMB blends at different Temp.
Figure-6: MSCR average recovery at 64 °C
Figure-7: Non-recoverable creep compliance (Jnr) at 64 °C

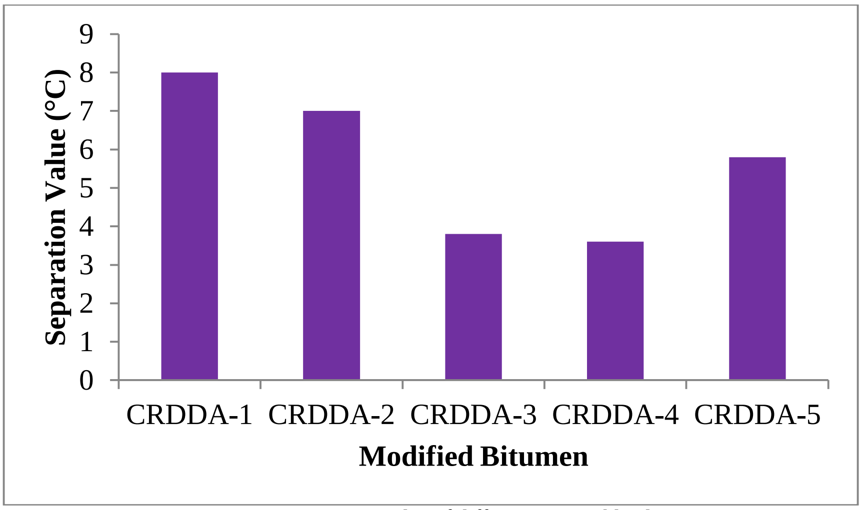

Figure-1: Separation value of different CRMB blends

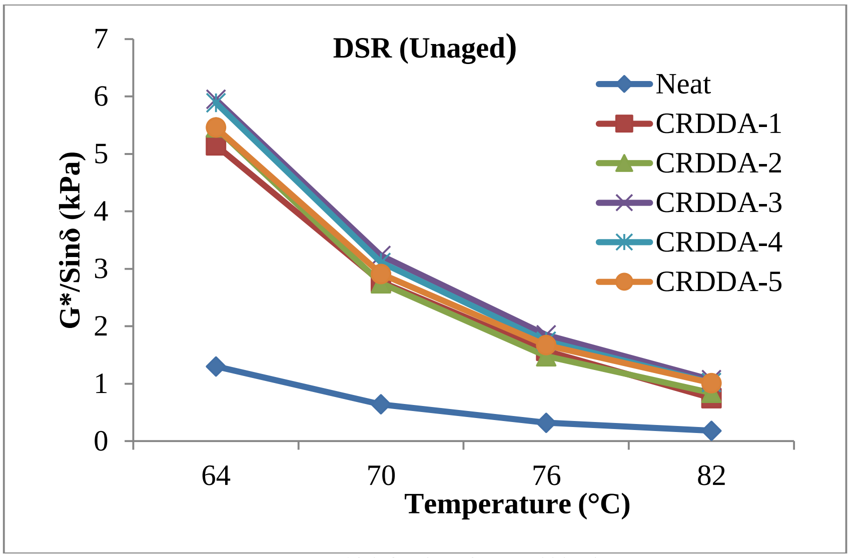

Figure-2: G*/Sinδ value of Unaged blends

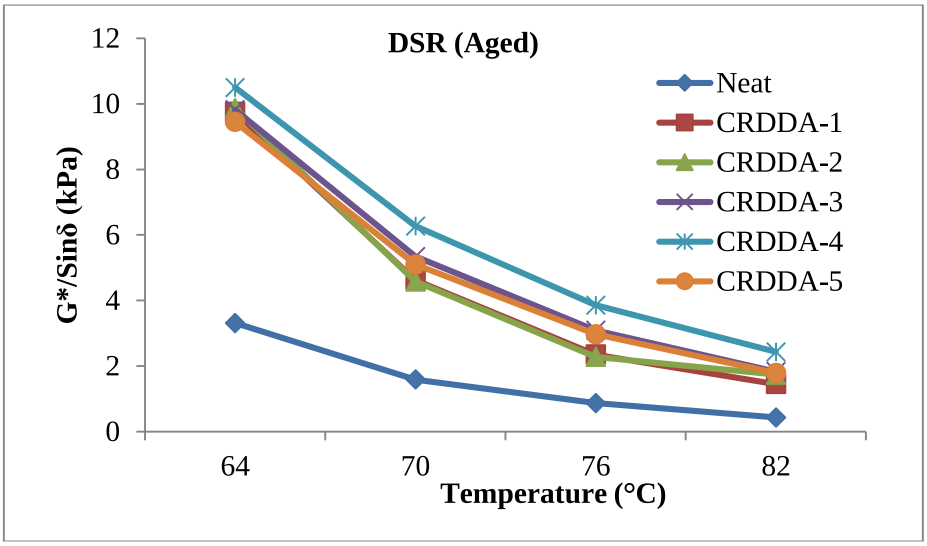

Figure-3: G*/Sinδ value of RTFO aged blends

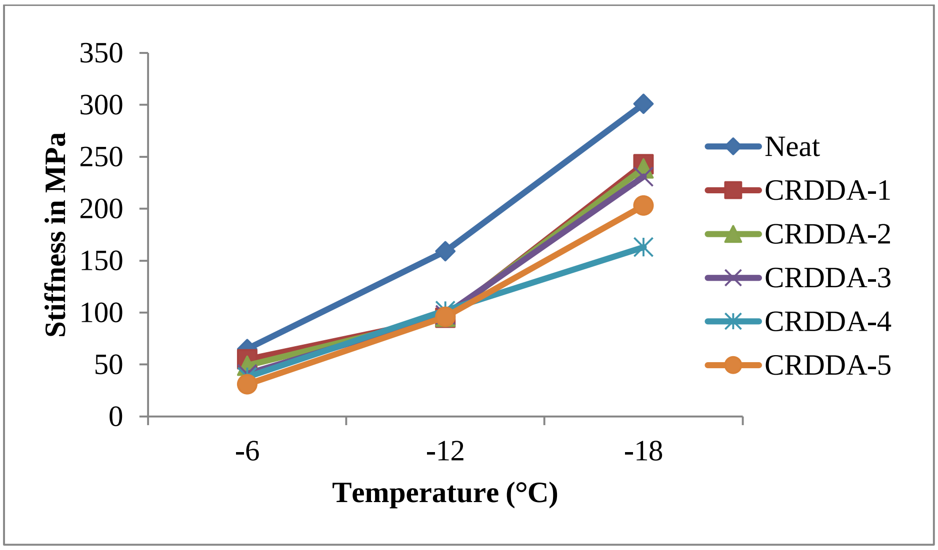

Figure-4: Stiffness of CRMB blends at different Temp.

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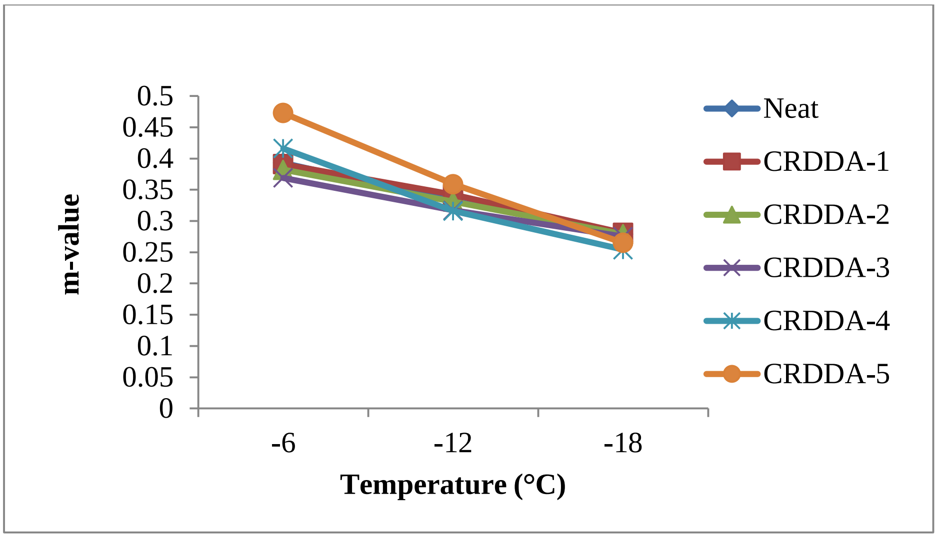

Figure-5: m-value of CRMB blends at different Temp.

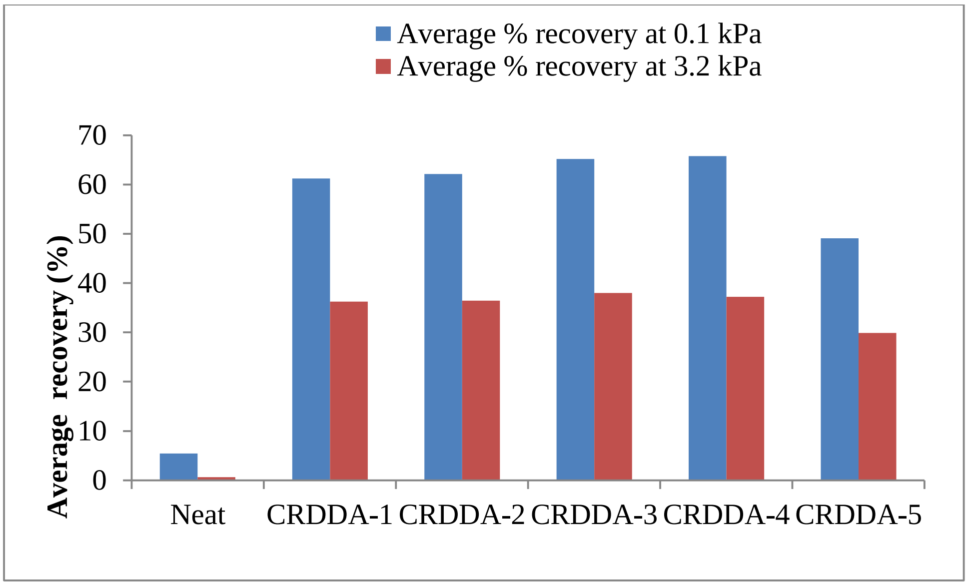

Figure-6: MSCR average recovery at 64 °C

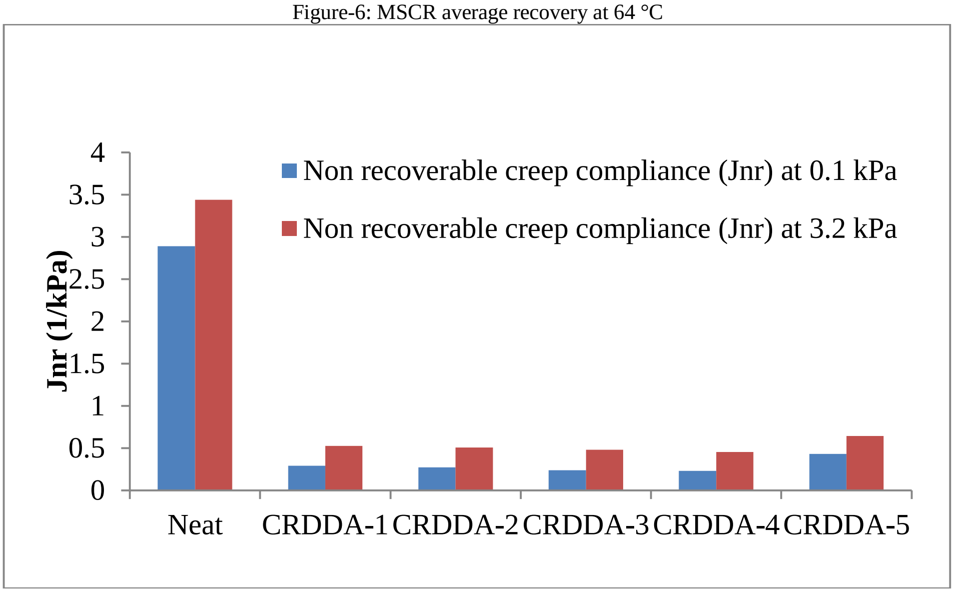

Figure-7: Non-recoverable creep compliance (Jnr) at 64 °C