Ultra Chemistry Vol. 8(1), 49-60 (2012).

Study on effects of polymer on properties of Bitumen

PRASHANT KUMAR[1], P. SENTHIVEL[2], BISWANATH SAHA[2]
and M. K. JHA[1]

[1]National Institute of Technology, Jalandhar - 144011, Punjab (INDIA)
[2]Bharat Petroleum Corporation Limited
Corporate Research and Development Centre Greater Noida

(Acceptance Date 21st January, 2012)

Abstract

Modification of base bitumen using additives, modifiers are required to overcome the pavement failures like permanent deformation, bleeding, cracking and water damage and to improve the functioning of bitumen mixtures and to facilitate day by day increasing traffic loadings in changing climatic conditions etc.

In the present work four polymer modified products were prepared with varying structure, molecular weight and weight percentage of polymer. Same VG 10 bitumen was used as base bitumen for the polymer modified bitumen (PMB) products. These products were evaluated as per IS 15462-2004 specification for PMB and comparison was done between different structured, different molecular weight and different weight percentage of polymer products for PMBs performance properties. The study concludes that Radial polymer with higher molecular weight and viscosities are best among the PMBs.

Key words: Polymer structure, Molecular Weight, Viscosity etc.

1.0 Introduction

Bitumen[1-7] is a mixture of organic liquids that are highly viscous, black, sticky, entirely soluble in carbon disulfide, and composed primarily of highly condensed polycyclic aromatic hydrocarbons used in road pavement and as water proofing agent in roofing. To facilitate day to day rising traffic loads in changing climatic conditions and to overcome the failures like permanent deformation, cracking and water damage, many important

Corresponding Author : Dr. M.K.Jha Professor and Head Department of Chemical Engineering
National Institute of Technology Jalandhar, Punjab (India)-144011
E-mail: jhamk@nitj.ac.in

steps has been taken to improve the functioning of bitumen mixtures. These steps lead to the basic variation in the design of bitumen pavements. For improving the bitumen characteristics, specific performance enhancers have been analyzed. These include additive modification, polymer modification and crumb rubber modification etc.[24]. Modified Binders are more stable under heavy loads, braking and accelerating forces and shows increased resistance to permanent deformation in hot weather. It resists fatigue loads and having better adhesion between aggregates and binders[8,9].

In general, addition of polymers to bitumen mixtures enhances the resistance of bitumen to fatigue cracking, rutting, temperature cracking and stripping. In polymer modification various types of additives are incorporated such as virgin polymers, recycled plastics, etc. Indeed polymer modified bitumen is emerging as one of the important construction materials for flexible pavement[10-20].

Straight run bitumen, the characteristics of which have been improved by addition of polymers, namely, styrene-butadiene-styrene (SBS), ethyl vinyl acetate (EVA) or polyethylene (PE) etc.

Styrene–butadiene styrene (SBS) is one of the most commonly used bitumen modifiers for paving applications[10] and is used in this study. Styrenic tri-block copolymers, commonly termed thermoplastic rubbers due to their ability to unite both elastic and thermoplastic properties, can be produced by a sequential operation of following polymerization of styrene butadiene styrene (SBS)[23-34].

Alternatively, a di-block precursor can be produced by successive polymerization of styrene and the midblock monomer butadiene, followed by a reaction with a coupling agent. So, not only linear copolymers but also multi-armed copolymers (known as star-shaped, radial or branched copolymers) can be produced. The structure of a SBS copolymer therefore consists of styrene butadiene styrene tri-block chains, having a two-phase morphology of spherical polystyrene block domains within a matrix of poly-butadiene[21].

SBS copolymers derive their strength and elasticity from physical cross-linking of the molecules into a three-dimensional network. The polystyrene end blocks impart the strength to the polymer while the poly-butadiene rubbery matrix mid-blocks give the material its outstanding elasticity. The efficiency of these cross-links diminishes rapidly above the glass transition temperature of polystyrene (approximately 100^{o}C), although the polystyrene domains will reform on cooling restoring the strength and elasticity of the copolymer[21,22].

As SBS is blended with bitumen, the elastomeric phase of the SBS copolymer absorbs the maltenes (oil fractions) from the bitumen and swells up to nine times its initial volume[21]. At appropriate SBS concentrations, a continuous polymer network (phase) is formed throughout the PMB, considerably modifying the bitumen properties. As thermoplastic rubbers have molecular weights similar to or higher than that of the asphaltenes, they compete for the solvency power of the maltene phase and phase separation can occur if inadequate maltenes are available. This phase separation is an sign of the incompatibility of the base bitumen and polymer and care should be taken when blending thermoplastic rubber PMBs. The compatibility of the SBS—bitumen blend can be enhanced through the addition of aromatic oils. However, too high an aromatic content in the blend will dissolve the polystyrene blocks and wipe out the benefits of the SBS copolymer[9-19].

Ageing of conventional bitumen, as well as PMBs, is induced by chemical and/or physical changes that take place during the production of the pavement and throughout its service life. Ageing (hardening) is primarily related with the loss of volatile components and oxidation of the bitumen during asphalt mixture construction (short-term ageing) and progressive oxidation of the in-place material in the field (long-term ageing). Both processes are usually accompanied by hardening of the binder, which general influences the deterioration of the bitumen pavement. Other factors may also contribute to ageing, such as molecular structuring over time (steric hardening) and actinic light (primarily ultraviolet radiation, particularly in desert conditions)[10].

The objectives of the present works are:

- To investigate the influence of polymer molecular weight, structure and polymer dosage on the performance properties of polymer modified bitumen
- To find out the most suitable polymer modifier for bitumen modification

2.0. Material and Methods

A VG10 viscosity grade base bitumen has been taken from BPCL refinery. In order to characterize the properties of the base bitumen, conventional test methods such as; penetration test, softening point test, ductility test, etc. were performed. These tests were conducted in conformity with the relevant test methods that are presented in Table 1.

Table 1 Properties of Base Bitumen (VG 10)

Sl. No.	Characteristics	Bitumen VG10	Specification of paving Bitumen Grade VG 10
1	Penetration at 25°C, 0.1 mm, 100g, 5s	86	80-100
2	Softening Point, (R&B), °C, Min	46	40
3	Viscosity @60°C, P, min	1481	800
4	Viscosity @135°C, cSt, min	310	250
5	TFOT		
a)	Loss in mass on heating, %	<1%	<1%
b)	Viscosity Ratio @ 60°C, max	1.71	4
c)	Ductility @ 25°C	>100 cm	>75 cm

Three SBS polymers were used in this study to modify the bitumen. The details are given below

Table 2. Polymer Modifiers properties

POLYMER/PROPERTIES	STRUCTURE	STYRENE (%)	BUTADIENE (%)	BROOKFIELD VISCOSITY
C.P.1	RADIAL	30	70	18500 CPS
C.P. 2	LINEAR	31	69	3900 CPS
C.P.-3	RADIAL	30	70	11100 CPS

For the preparation of modified bitumen samples IKA T50 homogenizer was used and rotated at the speed of 4000 rpm.Bitumen VG 10 was taken as base material to prepare PMB samples, pre-weight desired quantities, mixed together and added to bitumen at 170-180 ^{o}C and the mixture was kept under high speed shearing during mixing process for 3 hrs. Experiments were performed as per IS 15462:2004: Requirements of Polymer Modified Bitumen –Elastomeric[27-34].

3.0. Results and Discussion

In this study, polymers were used to modify the bitumen. The physical properties of base bitumen were evaluated as per IS 73:2006 and physical properties of base bitumen are given in Table 1. The physical properties of PMB, was evaluated as per IS 15462:2004 for polymer modified bitumen**.** The composition and name assigned to the product is given in table 3.

Table 3 Composition and Product name given

Composition (by weight)	Name Assigned to the Product
97 % VG10 Bitumen + 3% C.P.-1	PMB P-1
96 % VG10 Bitumen + 4% C.P.-1	PMB P-2
96 % VG10 Bitumen + 4% C.P.-2	PMB P-3
97 % VG10 Bitumen + 3% C.P.-3	PMB P-4

The characteristics of PMB, Elastomeric and Thermoplastic (type B) according to IS-15462:2004 specification is given in Table 4. The polymer modified bitumen containing 4 wt % polymer namely PMB P-2 and PMB P-3 characteristics were found to meet specification for PMB 40 type B and 3 wt % namely, PMB P-1 and PMB P-4 were found to meet specifi-cation for PMB 70 type B. The Results are discussed below-

Penetration :

Penetration test were performed on all the samples at 25 °C. The results showed that type of additives as well as polymers molecular weight and structure has effects on penetration of the product. It is also observed from Fig. 1 that the PMB P-1 shows 39.53%, PMB P-2 shows 44.1 %, PMB P-3 shows 39.53 %, and PMB P-4 shows 33.72 % decrease in the penetration as compared to base bitumen. The penetration values decrease slowly as weight percentage of the polymer increases. It is also observed that product prepared using high molecular weight polymer with same dosage (3 wt %) and radial structured polymer is showing low penetration values as compared to product prepared with low molecular weight polymer. The results show that the product prepared with radial structure polymer is showing less penetration than product prepare with linear polymer. This may be the fact that the radial structured polymer interacts better than linear polymer with base bitumen[11-20].

Softening Point (R&B) :

Softening Point (R&B) is the temperature at which bitumen sample began to flow. It is observed from figure 2 that using polymer or crumb rubber increases the softening point of the final product. Specifically PMB P-1 shows 26.1% increase, PMB P-2 shows 47.26 % increase, PMB P-3 shows 47.26 % increase and PMB P-4 shows 26.1 % increase in softening point temperature as compared to base bitumen. The softening point increases with increase in weight percentage of polymer and remains unaffected by the change of molecular weight and structure of the polymer for the polymer modified bitumen product[21-30].

Elastic Recovery :

It is observed from figure 3 that modified bitumen products which were made using elastomeric polymers shows good elasticity. Elastic recovery property depends upon tensile strength of the materials used. Specifically PMB P-1 shows 70% elastic recovery, PMB P-2 shows 89% elastic recovery, PMB P-3 shows 74 % elastic recovery and PMB P-4 shows 71% elastic recovery. The elastic recovery of the PMBs increases with increase in weight percentage of the polymer content. Molecular weight of the polymer shows a negligible effect on elastic recovery and higher molecular weight polymer products shows marginally better elasticity than less molecular weight products. From the results, it is observed that radial structured polymer product found to give better elastic recovery than that linear structured polymer product. This can be attributed to the fact that radial structured polymers have better tensile strength as compared to linear structured polymer, and also it has better chemical interaction with asphaltene molecules[31-34].

Rotational Viscosity:

Rotational viscosity is done to check the pumpability of the bitumen samples. It can be observed from fig. 4 rotational viscosity of base bitumen is low but modified bitumen product shows high viscosity and rotational viscosity of the base bitumen is measured at 135°C and for modified bitumen it is measured at 150 °C. Specific observations are that the viscosity of the bitumen increases with increase in weight percentage of polymer content. Expectedly, high molecular weight polymer products show more viscosity than low molecular weight polymer products. Radial polymer product shows much better result for rotational viscosity as compared to linear polymer product[15-34].

Separation Difference in Softening Points (R&B) :

Polymers have a tendency to settle down at the bottom of the container, and bitumen comes on top. The results are shown in figure 5. PMB P-1 has separation difference of 2 °C; PMB P-2 has separation difference of

1 °C, PMB P-3 has separation difference of 2 °C and PMB P-4 has separation difference of 2 °C in upper and top layer of bitumen. All the PMBs are showing good storage stability irrespective of their structure, polymer content and molecular weight[23-27].

Loss in mass on heating :

Loss in mass on heating is done by thin film oven test. Volatile matter evaporates in the TOFT as heating is done for 5 hours at 163 °C.

All the modified bitumen samples and unmodified bitumen sample show less than 1 percentage weight loss after TOFT. No noticeable variation is observed.

Increase in Softening Point, (R&B):

Increase in softening point test (R&B) is performed after TOFT. Softening point (R&B) increases after TOFT as volatile matter evaporates during the TOFT test. The results are shown in fig 6. In polymer modified bitumen sample had increment increase in softening point. PMB P-1 had an increment of 2°C; PMB P-2 had an increment of 3°C, PMB P-3 had an increment of 4 °C and PMB P-4 had an increment of 3°C in their softening point. In PMBs only PMB P-1 is showing excellent results. It is to note that the reference base bitumen had an increase in softening point of 4 °C.

Retention of Penetration :

This test is also performed after TOFT test. Base bitumen has the retained 47.67% of its penetration value after TOFT test. The results are shown in fig. 7, PMB P-1 has retained 6.12%, PMB P-2 has retained of 10.42 %, PMB P-3 has retained of 25%, and PMB P-4 has retained of 26.3% of their penetration value after TOFT test. Low weight percentage polymer product has retained more penetration values than high weight percentage polymer product (%w/w). It is also observed that high molecular weight polymer product performs better than low molecular weight a product which is explained from the data that low molecular weight polymer product retained more penetration value than high molecular weight polymer product. Radial structured polymer products are performing better than linear structured polymer products as linear structured polymer product has retained much more penetration than radial structured polymer[17-34].

Elastic Recovery of half thread in ductilometer at 25 ° C, %:

Elastic recovery test at 25°C is performed after TOFT. The results are shown in fig 8. Specifically PMB P-1 shows 59% elastic recovery, PMB P-2 shows 68% elastic recovery, PMB P-3 shows 60 % elastic recovery PMB P-4 shows 63% elastic recovery. As compared to results of elastic recovery at 15 °C, PMB P-1 lost its 15.71%, PMB P-2 lost its 22.47 %, PMB P-3 lost its 18.91% and PMB P-4 lost its 11.26% of elastic recovery when test performed after TOFT at 25°C. Less weight percentage of polymer content product has retained more elasticity than product with more weight percentage of polymer product. Low molecular weight product has lost less than high molecular weight product has lost more as compared to it. Linear polymer product has lost less elasticity as compared to high molecular weight product[1-15].

Table 4. IS 15462:2004: Requirements of Polymer Modified Bitumen –Elastomeric Thermoplastic Based – Type-B

S. No.	Characteristics	PMB-70	PMB-40	TEST METHOD	REFERENCE NO./ANNIX
i)	Penetration at 25° C, 0.1 mm, 100g, 5 Sec.	50-90	30-50	IS-1203	-
ii)	Softening Point, (R&B), °C,Min	55	60	IS-1205	-
iii)	Fraass Breaking Point,* °C, Max	-16	-12	IS-9381	-
iv)	Flash Point, COC,°C ,Min	220	220	IS-1209	-
v)	Elastic recovery of half Thread in Ductilometer at 15° C ,%, Min	70	70	-	A
vi)	Separation, Difference in Softening Point, R & B, °C, Max	3	3	-	B
vii)	Viscosity at 150°C, P (RV)	2 TO 6	3 TO 9	IS-1206 (Part-1)	-
viii)	*Thin Film Oven Tests and Test on Residue*				
a)	Loss on weight ,%, Max	<1%	<1%	IS-9382	-
b)	Increase in softening Point, °C, Max	6	5	-	B
c)	Reduction in penetration of residue, at 25°C, % Max	35%	35%	IS-1203	-
d)	Elastic recovery of half Thread in ductilometer at 25°C , % Min	50	50	-	B

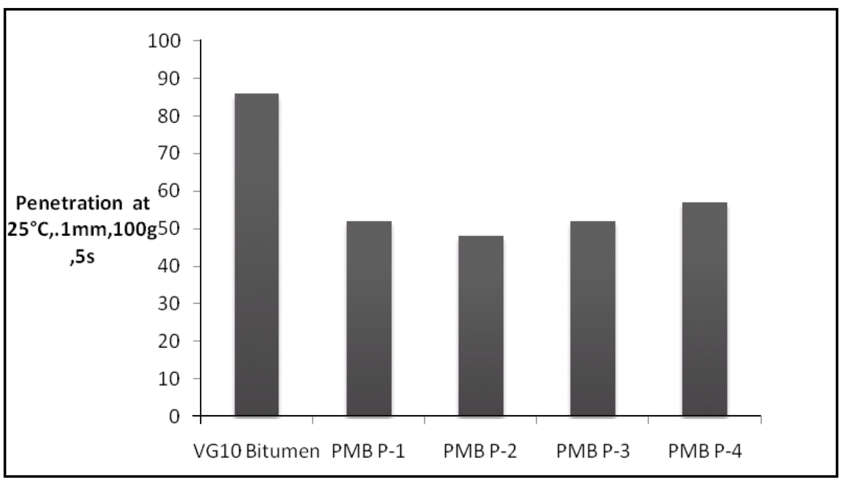

Fig 1. Penetration Test Results for base bitumen, PMB samples

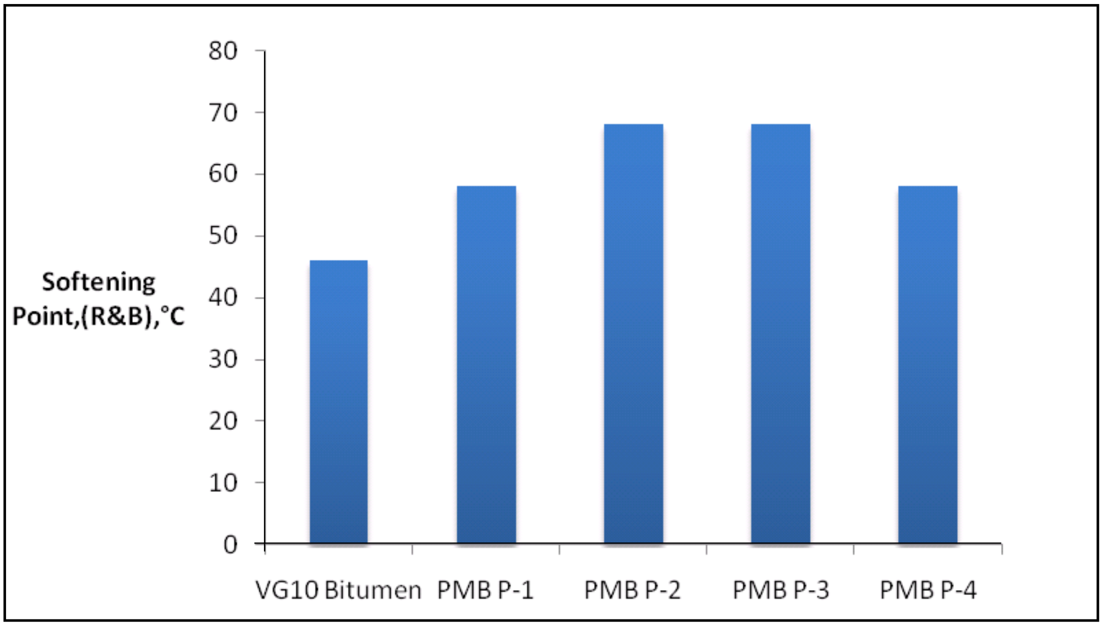

Fig. 2. R&B Softening Point Test Results for base bitumen, PMB samples

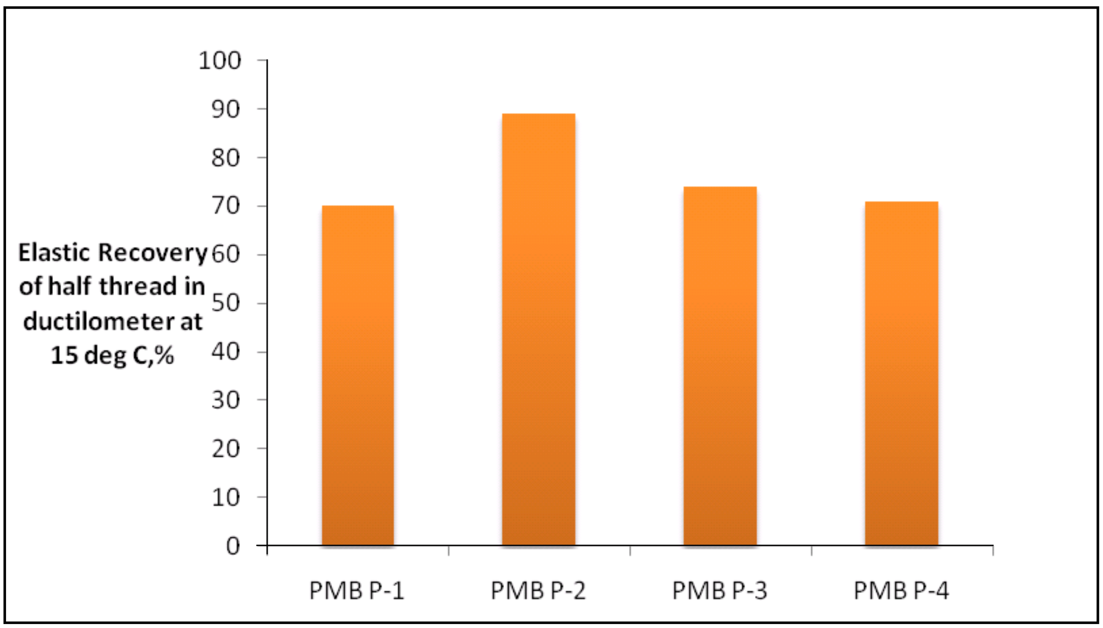

Fig 3. Elastic Recovery of half thread in ductilometer at 15^{o}C,
Test Results for PMB samples

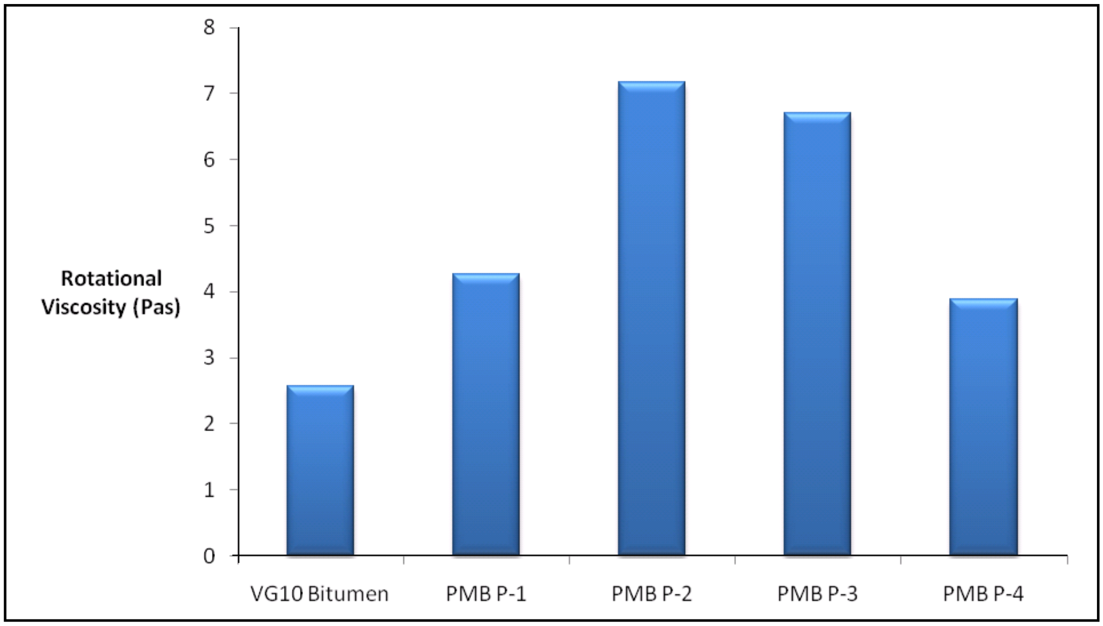

Fig. 4.Rotational Viscosity Test Results for Base Bitumen, PMB samples

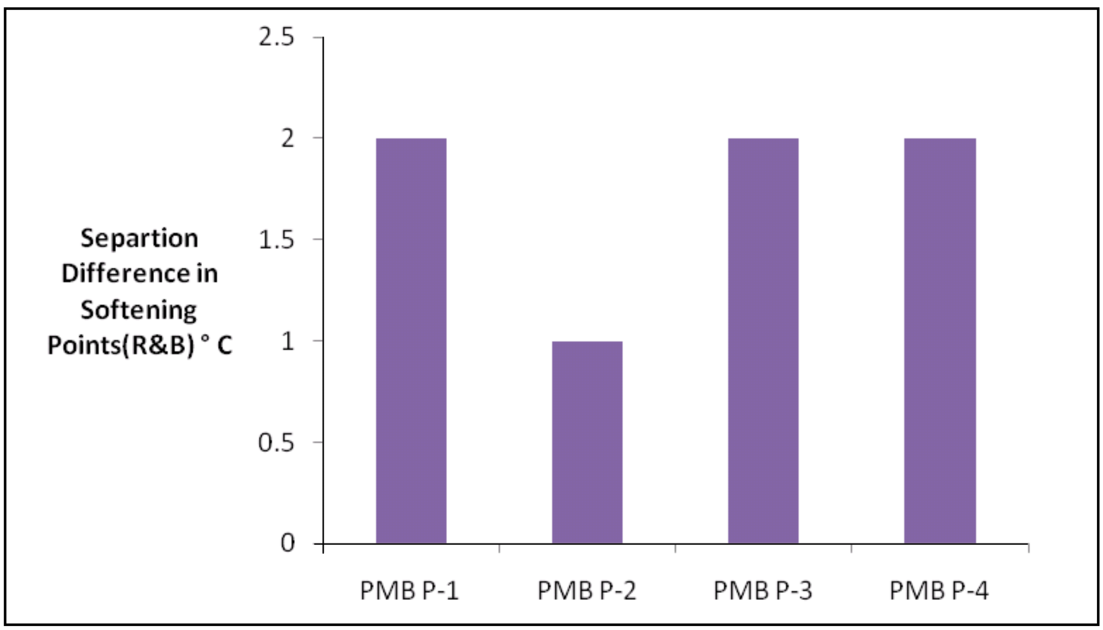

Fig. 5. Separtion Difference in Softening Point (R&B) °C, Test Results for PMB samples

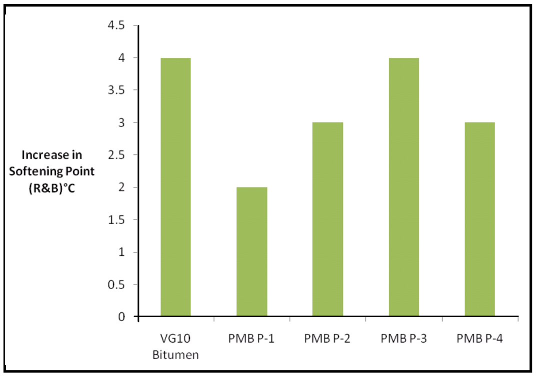

Fig. 6. Increase in Softening Point,(R&B), °C Max, Test Results for Base Bitumen, PMB

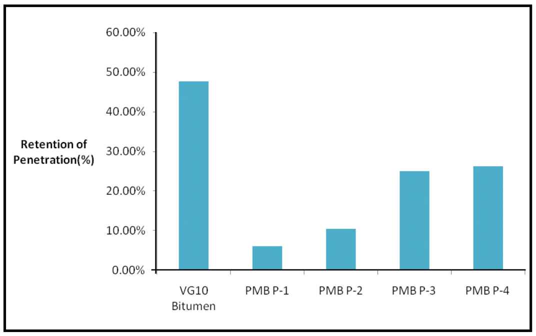

Fig. 7. Retention of Penetration (%), Test Results for Base Bitumen, PMB samples

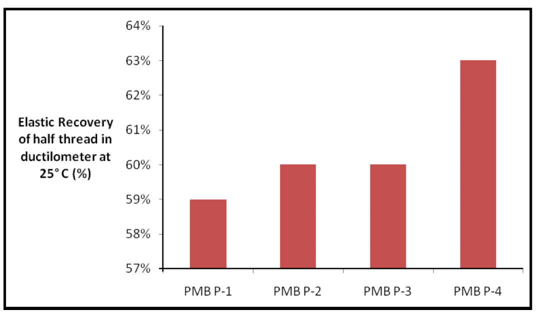

Fig. 8. Elastic Recovery of half thread in ductilometer at 25° C (%), Test Results for PMB samples

5.0 Conclusions

Following conclusions were drawn from this present investigation:

- The modification of VG 10 bitumen with polymers enabled to improve the properties of bitumen which in turn meet the severe requirements of increased performance at application end
- The result shows that the blend of VG 10 bitumen and 3 wt% C.P.-1 and 3 wt% C.P.-3 upgraded to PMB-70 type B grades according to IS 15462:2004 specifications
- The result shows that the blend of VG 10 bitumen and 4 wt% C.P.-1 and 4 wt% C.P.-3 upgraded to PMB-40 type B grades according to IS 15462:2004 specifications
- It was found that product containing 4% polymer performed better than 3% polymer. It is to mention that same commercial polymer was used as additive in both cases
- Radial structured polymer product gives much better performance properties than linear one
- High molecular weight polymer products give much better performance properties than low molecular weight polymer products
- From the study it is observed that radial polymer with high molecular weight will be the most suitable polymer for modification of bitumen

References

1. http://en.wikipedia.org/wiki/Bitumen viewed on 24/4/2010
2. http://www.sulphurinstitute.org/learnmore/faq.cfm viewed on 23/5/2010
3. http://www.irc.org.in/editorials/2005/june.htm viewed on 27/5/2010

4. http://www.sabita.co.za/documents/LIC%2021%20Crack%20Sealing%20hot%20modified.pdf viewed on 29/5/2010
5. http://www.scribd.com/doc/25385642/Bitumen-1viewed on 24/4/2010
6. http://en.unicarbide.com/news/pdf/ElvaloyAlgeria.PDF viewed on 26/04/2010
7. http://www.irc.org.in/editorials/2005/june.htm viewed on 26/5/2010
8. http://pavementinteractive.org/index.php?title=Pavement_History, viewed on 5/5/2010
9. http://eprints.usm.my/8676/1/A_STUDY_ON_THE_PHYSICAL_AND_MECHANICAL_PROPERTIES_OF_ASPHALTIC_CONCRETE_INCORPORATING_CRUMB_RUBBER_PRODUCED_THROUGH_DRY_PROCESS.pdf viewed on 12/5/2010
10. Airey Gordon D. and Rahimzade Behzad Combined bituminous binder and mixture linear rheological properties, *Construction and Building Materials* Volume *18,* Issue *7,* September, Pages 535-548 (2004).
11. Alrey G. D. Styrene butadiene styrene polymer modification of road bitumen, *Journal of Materials Science 39,* 951– 959 (2004).
12. AAPA, 2004. Australian Asphalt Pavement Association website www.aapa.asn.au. viewed on 5/5/2010
13. Anderson D.A., Maurer D., Ramirez T., Christensen D.W., Marasteanu M.O., Mehta Y. Field performance of modified asphalt binders evaluated with superpave test methods: I-80 test project. *Transportation Research Record;* 1661:60–8 (1999).
14. Bahia H.U., Perdomo D., Turner P. Applicability of Superpave binder testing protocols to modified binders. *Transportation Research Record;* 1586: 16–23 (1997).
15. Brule, B., "Polymer-Modified Asphalt Cements Used in the Road Construction Industry: Basic Principles,*Transportation Research Record 1535,* TRB, National Research Council, Washington, D.C. (1996).
16. Caltrans "Asphalt Rubber Usage Guide" *California Department of Transportation,* www.dot.ca.gov. viewed on 16/5/2010 (2003).
17. Chehovitts, J.G., "Binder Design Procedures", Federal Highway Administration, Crumb Rubber Modifier Workshop Manual, March (1993).
18. Collins J. Thermoplastic blocks copolymers for the enhancement of asphaltic binders in paving applications. Presented at the Paving and Transportation Conference, Albuquerque, NM, (1986).
19. Khandal Prithvi Singh "Quality Control Requirements for using Crumb Rubber Modified Bitumen (CRMB) in Bituminous mixtures" Journal of the Indian Roads Congress, Volume 67-1, April-June (2006).
20. King G. *et al*. Additives in asphalt. *Journal Assoc Asphalt Paving Technol A; 68,* 32–69 (1999).
21. Lu X. Isacsson U., Testing and appraisal of polymer modified road bitumens: State of the art. *Material and Structure; 28,* 139–59 (1995).
22. Lu X. Isacsson U., Compatibility and storage stability of styrene-butadiene styrene copolymer modified bitumens, Materials and Structures et Constructions, Vol. 30, December, pp 618-626 (1997).
23. Isacsson U, Lu X. Characterization of bitumens modified with SEBS, EVA and EBA polymers. *Journal of Material Science; 34,* 3737–45 (1999).
24. Lu X., Isacsson U,. Characterization of

bitumens modified with SEBS, EVA and EBA polymers. Journal Material Science; *34,* 3737–45 (1999).

25. Newcomb D. Limit the strain at the bottom of an asphalt pavement, and what do you get A perpetual pavement. *Hot Mix Asphalt Technol; 8(6),* 30–2 (2003).
26. Oliver, Aiderson, Tredrea and Karim. APRG Report No. 12 Results of the laboratory program associated with the ALF asphalt deformation trial. ARRB Transport Research (1995).
27. Roberts, F. L., P.S. Kandhal, E.R. Brown, D.Y. Lee, and T.W. Kennedy, "Hot Mix Asphalt materials, Mix Design and Construction", HMA Textbook, NAPA Education foundation, (1996).
28. S. Kim, S.W. Loh, H. Zhai, and H.U. Bahia, "Advanced Characterization of Crumb Rubber-Modified Asphalts, using Protocols Developed for Complex Binders", Transportation Research Record 1767. Washington, D.C.: *Transportation Research Board,* pp. 15–24 (2001).
29. Sassan Aflaki, Nader Tabatabaee, Proposals for modification of Iranian bitumen to meet the climatic requirements of Iran, *Construction and Building Materials 23,* 2141–2150 (2009).
30. Sebaaly P.E., Bazi G.M., Vivekanathan Y. Evaluation of new pavement technologies in Nevada, University of Nevada, (2003).
31. Terrel R, Walter J. Modified asphalt pavement materials: The European experience. *Journal Association Asphalt Paving Technol; 55,* 482 (1986).
32. Thompson D.C. Hoiberg A.J., editor. Bituminous materials: Asphalt tars and pitches. Robert Krieger Publishing Co.; (1979).
33. Whiteoak D., Read J.M. The Shell bitumen handbook. London: Thomas Telford Services Ltd.; (2003).
34. Y. Yildirim, "Polymer Modified Asphalt Binders", *Journal of Construction and Building Materials,* Elsevier, (2005).